

# Ion-Pairing Control of Excited-State Electron-Transfer Reactions. Quenching, Charge Recombination, and Back Electron Transfer

Catherine D. Clark and Morton Z. Hoffman\*

Department of Chemistry, Boston University, Boston, Massachusetts 02215

Received: December 18, 1995; In Final Form: February 13, 1996<sup>⊗</sup>

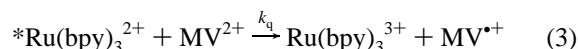
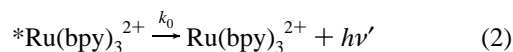
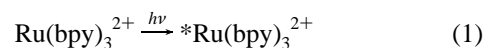
The rate constants for the oxidative quenching of  $^*\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{MV}^{2+}$  ( $k_q$ ) and the charge recombination reaction between  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{MV}^{•+}$  in bulk solution ( $k_{\text{rec}}$ ) and the cage escape yields of the redox products ( $\eta_{\text{ce}}$ ) were determined as a function of added electrolytes ( $\text{Na}^+$  salts of oxyanions and halides) and temperature (10–60 °C) in aqueous solution. At 25 °C and constant [anion],  $k_q$  and  $k_{\text{rec}}$  are a function of the specific anion, decreasing in the order  $\text{ClO}_4^- \gg \text{SO}_4^{2-} \sim \text{HPO}_4^{2-} > \text{H}_2\text{PO}_4^- \sim \text{CH}_3\text{CO}_2^-$  and  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ . Activation energies for  $k_q$  and  $k_{\text{rec}}$  for  $\text{ClO}_4^-$  are  $\sim 30\%$  lower than the average values for the other salts. Values of  $\eta_{\text{ce}}$  show anion-specific trends opposite to those for  $k_q$  and  $k_{\text{rec}}$ . The reactant cations are extensively ion-paired by the dominant anions in bulk solution, and a similar situation is proposed to exist within the quenching solvent cage. The electron-transfer component of quenching for ion-paired species ( $k_{\text{ip}}$ ) was extracted from  $k_q$  by use of the Olson–Simonsen treatment;  $\Delta H^\ddagger$  (activation enthalpy) and  $\lambda$  (solvent reorganization energy) were evaluated for  $k_{\text{ip}}$  and back electron transfer within the solvent cage ( $k_{\text{bt}}$ ) and were found to be smallest for  $\text{ClO}_4^-$  and  $\text{I}^-$ . The correlation that exists between  $k_{\text{ip}}$  or  $k_{\text{bt}}$  and the standard free energy of hydration ( $\Delta G^\circ_{\text{hyd}}$ ) of the anions indicates that the rates of electron transfer between the cationic reactants are greatest in the presence of anions that have the most weakly-held hydration sphere and the greatest ability to break the water structure. The rate constants of quenching and charge recombination and the yields of redox products can be fine-tuned through the variation of the supporting electrolyte as well as the variation of temperature and ionic strength.

## Introduction

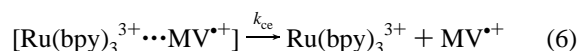
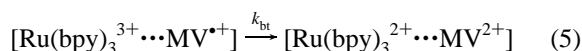
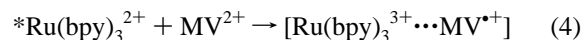
The transfer of an electron between donor and acceptor sites on the same or other species in fluid media results in the reorganization of the solvent molecules that form the “cage” within which the reaction occurs. The energy involved in the solvent reorganization is an important quantity that controls the rate of the intra- or intermolecular electron-transfer reaction. When the reacting moieties are charged, the reorganization of the paired counterions and the solvent molecules associated with them will contribute another component to the energetics and kinetics of the reaction. At issue is whether that component is ion specific; if it is, another parameter can be introduced into the fine-tuning of the rates of electron transfer.

Photoinduced electron-transfer quenching of the excited states of charged transition-metal coordination complexes offers the opportunity to examine ion-pairing control of the bimolecular quenching reaction, the bimolecular charge recombination reaction between the redox products in bulk solution, and the intramolecular back-electron-transfer reaction of the geminate pair within the quenching solvent cage. Because it still serves as the paradigm of electron-transfer quenching, we have chosen the reaction between the MLCT excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine) and methylviologen ( $N,N'$ -dimethyl-2,2'-bipyridinium cation;  $\text{MV}^{2+}$ ) in aqueous solution as the object of our examination.

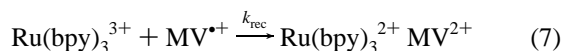
Upon the excitation of  $\text{Ru}(\text{bpy})_3^{2+}$  (reaction 1),  $^*\text{Ru}(\text{bpy})_3^{2+}$ , in competition with its natural radiative and nonradiative decays (reaction 2), is oxidatively quenched by  $\text{MV}^{2+}$  (reaction 3), generating  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{MV}^{•+}$  in bulk solution.



The quantum yield of the redox products released into solution ( $\Phi$ ) is given by the expression  $\Phi = \eta^* \eta_q \eta_{\text{ce}}$ , where  $\eta^*$  is the efficiency of formation of  $^*\text{Ru}(\text{bpy})_3^{2+}$  in the excitation process ( $\sim 1$ ),<sup>1</sup>  $\eta_q$  is the efficiency of the quenching of the excited state ( $\eta_q = k_q[\text{MV}^{2+}]/(k_q[\text{MV}^{2+}] + k_0)$ ), and  $\eta_{\text{ce}}$  is the efficiency of the escape of the redox products from the quenching solvent cage. According to the conventional cage escape model,<sup>2</sup> the formation of the geminate redox pair (reaction 4) is followed by competitive intramolecular back electron transfer (reaction 5) and diffusional cage escape (reaction 6);  $\eta_{\text{ce}} = k_{\text{ce}}/(k_{\text{ce}} + k_{\text{bt}})$ .



The redox pair in bulk solution can subsequently engage in electron-transfer charge recombination, regenerating the starting species in their ground states (reaction 7).



<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, April 1, 1996.

Inasmuch as the inter- and intramolecular processes involve ionic species, their rate constants are functions of the ionic strength ( $\mu$ ) of the solution; for intermolecular reactions of the same charge type, as is the case here, an increase in  $\mu$  causes an increase in the values of  $k_q$  and  $k_{\text{rec}}$ .<sup>3</sup> At the same time, an increase in  $\mu$  reduces the rate at which the ions diffuse apart, decreasing  $k_{\text{ce}}$  and decreasing  $\eta_{\text{ce}}$ .<sup>4</sup> However, Olson and Simonson<sup>5</sup> noted in their study of the effect of the presence of "inert" salts on the reaction rate between ions of like charge that the variations in the rate constants were almost exclusively due to the concentration and nature of the oppositely-charged salt ions rather than  $\mu$ .

There have been several recent reports of specific salt effects in various inter- and intramolecular electron-transfer reactions<sup>6</sup> and a few on the  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$  system. In one of the first systematic studies, Gaines<sup>7</sup> noted the accelerating effect of  $\text{NaClO}_4$  (compared to  $\text{NaCl}$ ) on  $k_q$ . Kalyanasundaram and Neumann-Spallart<sup>8</sup> measured  $k_q$ ,  $k_{\text{rec}}$ , and  $\eta_{\text{ce}}$  in the presence of  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaClO}_4$ . Although their values were measured at different ionic strengths, making direct comparison difficult,  $\eta_{\text{ce}}$  appeared to be strongly dependent on the nature of the anion. Ochiai et al.<sup>9</sup> studied the effect of  $\text{LiI}$ ,  $\text{LiCl}$ , and  $\text{KI}$  on  $k_q$ ; no differences were observed for  $\text{LiI}$  and  $\text{KI}$ , but  $k_q$  was higher in the presence of  $\text{LiI}$  compared to  $\text{LiCl}$ ; the results were interpreted in terms of ion-pair formation and solvation-desolvation effects. Most recently, Scandola and co-workers<sup>10</sup> examined  $k_q$  and  $k_{\text{rec}}$  as a function of  $\mu$  for solutions containing  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{NaClO}_4$ ; the acceleration of the rates due to  $\text{NaClO}_4$  was again noted, as well as the lack of an effect upon changing cations. This specific anion effect was attributed to changes in the unimolecular electron-transfer steps, rather than in diffusion rates, and was ascribed to differences in the hydrophobicity of the anions.

As part of our continuing investigation of the factors that affect the yields of energetic charge-separated species upon the electron-transfer quenching of photosensitizers,<sup>11</sup> we have examined the dependencies of  $k_q$ ,  $k_{\text{rec}}$ , and  $\eta_{\text{ce}}$  on temperature and the concentration of added electrolytes in aqueous solution. For the effect of specific anions, we chose the  $\text{Na}^+$  salts of the halides ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) and oxyanions that have similar tetrahedral structures ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ );  $\text{CH}_3\text{CO}_2^-$  was included because of its frequent use as a buffer. We were particularly interested in elucidating the specific "accelerating" effect of  $\text{ClO}_4^-$  that had been previously noted.

## Experimental Section

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  (GFS Chemicals) was recrystallized from water and dried over silica gel. Methylviologen dichloride (Aldrich) was recrystallized several times from methanol and dried under vacuum for over 24 h.  $\text{NaClO}_4$ ,  $\text{NaF}$  (GFS Chemicals),  $\text{Na}(\text{CH}_3\text{CO}_2)$  (Fisher),  $\text{Na}_2\text{SO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaCl}$  (Johnson Matthey Chemicals, Puratronic),  $\text{NaBr}$ , and  $\text{NaI}$  (Fluka) (all >99.5% purity) were oven-dried at 150 °C for over 10 h and stored in a desiccator. Distilled water was further purified by passage through a Millipore purification train.

Cyclic voltammetry measurements were performed on aqueous solutions at 25 °C with an EG&G 273A potentiostat and glassy carbon working electrode, Pt wire counter electrode, and  $\text{Ag}/\text{AgCl}$  reference electrode at a scan rate of 100 mV/s. The concentration of the supporting 1:1 electrolyte was 0.1 M.

Absorption spectra were measured with a diode array spectrophotometer (Hewlett-Packard 8452A). Transient absorption and emission measurements were made with a pulsed Nd:YAG laser (Quantel YG581) with excitation at 532 nm, the details of which have been described before.<sup>12</sup> A red filter was placed

in front of the monochromator (Instruments SA) in the emission measurements; a pulsed 150-W Xe lamp, perpendicular to the 7-ns exciting pulse, was used as the analyzing light in the absorption mode. The output voltage of the photomultiplier (Hamamatsu R928) was controlled to produce a linear response. The data were averaged for 10 and 20 shots for absorption and emission measurements, respectively. The temperatures of the solutions were controlled to  $\pm 0.1$  °C over the 10–60 °C range.

All solutions were contained in  $2 \times 1$ -cm laser cells, excited along the shorter path and analyzed along the longer path. Solutions could be deaerated before excitation by purging with Ar for 20 min. Ionic strengths were adjusted with appropriate concentrations of the salts. Quenching experiments were carried out on air-equilibrated or deaerated solutions ( $[\text{Ru}(\text{bpy})_3^{2+}] = 45 \mu\text{M}$ ); the values of  $k_q$  with estimated errors of  $\pm 5\%$  were obtained from slopes of the plots of the observed first-order rate constants for the decay of the emission from  $^*\text{Ru}(\text{bpy})_3^{2+}$  ( $\lambda = 605 \text{ nm}$ ) as a function of  $[\text{MV}^{2+}]$  (0.5–10 mM) for four or five different quencher concentrations at each electrolyte concentration. Values of  $k_{\text{rec}}$  were measured by monitoring the second-order decay of the absorption of  $\text{MV}^{\bullet+}$  at 605 nm ( $\epsilon_{605} = 1.37 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>13</sup> for deaerated solutions containing  $40 \mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and 2 mM  $\text{MV}^{2+}$ ; measurements for three duplicate solutions were averaged with an estimated error of  $\pm 10\%$ .

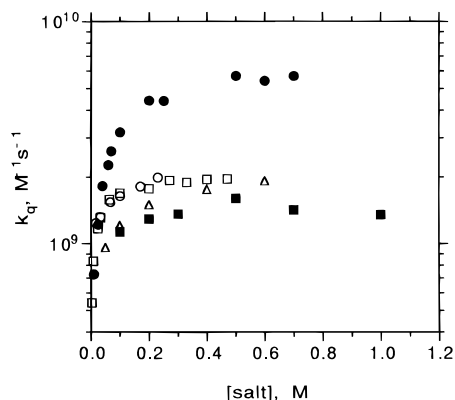
The quantum yield of redox products in bulk solution is a measure of the number of redox equivalents generated per photon absorbed; inasmuch as  $\eta^* \sim 1$ ,  $\Phi = \Delta[\text{MV}^{\bullet+}]/\Delta[^*\text{Ru}(\text{bpy})_3^{2+}]$ .  $\Delta[\text{MV}^{\bullet+}]$  and  $\Delta[^*\text{Ru}(\text{bpy})_3^{2+}]$  were obtained through an application of Beer's law ( $\Delta A = \epsilon_l l \Delta[c]$ ) from  $\Delta A$  at 605 nm (at 5–10  $\mu\text{s}$  after the laser pulse) and 450 nm (at  $t = 0$  for solutions containing only  $\text{Ru}(\text{bpy})_3^{2+}$  with the same absorbance at 532 nm as with quencher present), respectively;  $l = 2 \text{ cm}$ ,  $\epsilon_{605}$  is the value for  $\text{MV}^{\bullet+}$ , and  $\epsilon_{450}$  ( $-1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) represents the difference in the  $\epsilon$  values of the excited and ground states of  $\text{Ru}(\text{bpy})_3^{2+}$  at 450 nm.<sup>14</sup> Values of  $\eta_{\text{ce}}$  (estimated error  $\pm 7.5\%$ ) were calculated for solutions containing  $45 \mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and  $\leq 5 \text{ mM}$   $\text{MV}^{2+}$  from the slopes of linear plots of  $\Phi$  vs  $\eta_q$  or by averaging  $\eta_{\text{ce}}$  values obtained from three to five duplicate solutions with 2 mM  $\text{MV}^{2+}$ ;  $\eta_q$  was calculated from  $(k_{\text{obs}} - k_0)/k_{\text{obs}}$ , where  $k_{\text{obs}}$  is the observed first-order rate constant in the presence of  $\text{MV}^{2+}$ .

## Results

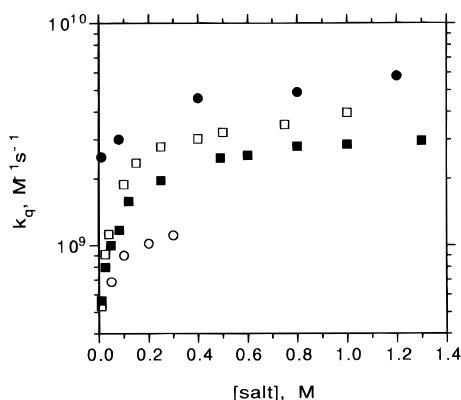
The presence of the background electrolytes had no effect on the absorption or emission spectra of the complex nor on the excited-state lifetime of  $^*\text{Ru}(\text{bpy})_3^{2+}$  in the absence of air ( $\tau_0 = 1/k_0$ ); at the concentrations of  $\text{MV}^{2+}$  used in this study, no change in its absorption was evident. Reversible potentials from the cyclic voltammetry experiments were +1.26 V for  $\text{Ru}(\text{bpy})_3^{3+/2+}$  and -0.45 V for  $\text{MV}^{2+/\bullet+}$  vs NHE, irrespective of the nature of the univalent electrolyte; the observed small variations of 10–20 mV with the different electrolytes are within the experimental error.

The values of  $k_q$ ,  $k_{\text{rec}}$ , and  $\eta_{\text{ce}}$  obtained as a function of temperature and the concentration of added electrolyte are given in the supporting information (see paragraph at the end of the paper).

Figures 1 and 2 show plots of  $k_q$  vs [salt] for the  $\text{Na}^+$  salts of the oxyanions and halides at 25 °C. The general increase in  $k_q$  toward a plateau value as [salt], and, hence,  $\mu$ , is increased is clearly in evidence. It is also clear that the value of  $k_q$  is a function of the specific anion; in particular,  $\text{ClO}_4^-$  enhances the rate relative to  $\text{H}_2\text{PO}_4^-$ -containing solutions, and  $k_q$  is significantly greater in the presence of  $\text{I}^-$  than  $\text{F}^-$ .



**Figure 1.** Values of  $k_q$  as a function of the concentration of  $\text{Na}^+$  salts of oxyanions at 25 °C:  $\text{NaClO}_4$  (●),  $\text{Na}_2\text{SO}_4$  (□),  $\text{NaH}_2\text{PO}_4$  (■),  $\text{Na}_2\text{HPO}_4$  (○),  $\text{Na}(\text{CH}_3\text{CO}_2)$  (△).



**Figure 2.** Values of  $k_q$  as a function of the concentration of  $\text{Na}^+$  salts of halide anions at 25 °C:  $\text{NaF}$  (○),  $\text{NaCl}$  (■),  $\text{NaBr}$  (□),  $\text{NaI}$  (●).

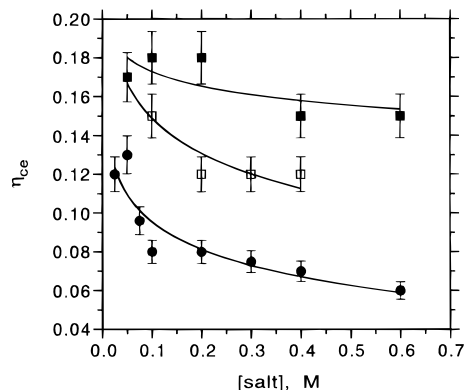
The second-order reaction between  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{MV}^{•+}$  extends well into the submillisecond time frame, making  $k_{\text{rec}}$  more difficult to obtain and, therefore, of lower precision. Nevertheless,  $k_{\text{rec}}$  exhibits the same general trend as seen for  $k_q$ ;  $\text{ClO}_4^-$  enhances the rate significantly, while  $\text{H}_2\text{PO}_4^-$  has the least effect.

As expected,  $k_q$  and  $k_{\text{rec}}$  are positive functions of temperature. Plots of  $\log k_q$  and  $\log k_{\text{rec}}$  vs  $1/T$  are linear for all added electrolytes. The values of  $E_a$  for  $k_q$  and  $k_{\text{rec}}$  (see supporting information) in the presence of  $\text{ClO}_4^-$  (11 and 10 kJ/mol, respectively) are lower than the corresponding average values in the presence of the other oxyanions (16 and 16 kJ/mol, respectively). The values of  $E_a$  are independent of the concentration of the electrolyte.

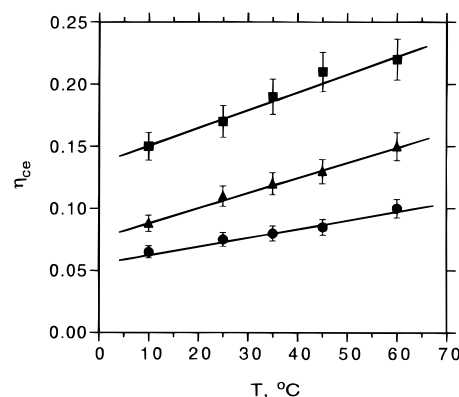
As has been demonstrated before for the oxidative quenching of  $^*\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{MV}^{2+}$ , the values of  $\eta_{\text{ce}}$  decrease with increased  $\mu$  and increase with increased temperature.<sup>15</sup> The values of  $\eta_{\text{ce}}$  are similar but certainly distinguishable outside the experimental error; in particular,  $\eta_{\text{ce}}$  is significantly lower for  $\text{ClO}_4^-$ . Figure 3 displays the concentration dependence data for  $\text{NaClO}_4$ ,  $\text{NaH}_2\text{PO}_4$ , and  $\text{NaCl}$ ; Figure 4 shows the temperature dependence for  $[\text{NaClO}_4] = 0.30 \text{ M}$ ,  $[\text{NaBr}] = 0.2 \text{ M}$ , and  $[\text{NaH}_2\text{PO}_4] = 0.05 \text{ M}$ , concentrations chosen in order to emphasize the effect. For reference, the value of  $\eta_{\text{ce}}$  obtained at 25 °C in the absence of any added electrolyte is 0.20.

## Discussion

**Quenching and Charge Recombination.** The results show clearly that  $k_q$  for the reaction between  $^*\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  and  $k_{\text{rec}}$  for the reaction between  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{MV}^{•+}$  are dependent on the specific anions present. The data will now



**Figure 3.** Values of  $\eta_{\text{ce}}$  as a function of  $[\text{salt}]$  at 25 °C for  $\text{NaClO}_4$  (●),  $\text{NaH}_2\text{PO}_4$  (■), and  $\text{NaCl}$  (□). Error bars:  $\pm 7.5\%$ .



**Figure 4.** Values of  $\eta_{\text{ce}}$  as a function of temperature for  $\text{NaClO}_4$  (●) at  $\mu = 0.30 \text{ M}$ ,  $\text{NaBr}$  (▲) at  $\mu = 0.2 \text{ M}$ , and  $\text{NaH}_2\text{PO}_4$  (■) at  $\mu = 0.05 \text{ M}$ . Error bars:  $\pm 7.5\%$ .

be treated in a number of ways in order to account for the trends as a function of  $\mu$  and  $T$ . Because the data for  $k_q$  are so much more reliable than those for  $k_{\text{rec}}$ , the various treatments will be applied specifically to  $k_q$ ; the similarity of the trends for both rate constants suggests that the conclusions reached for  $k_q$  can be applied equally well to  $k_{\text{rec}}$ .

**A. Debye–Hückel Treatment.** The most widely used framework for the discussion of reaction rate constants in solutions of electrolytes is the extended Debye–Hückel theory;<sup>16</sup> in eq 8,  $k$  is the observed rate constant,  $k_0$  is the rate constant

$$\log k = \log k_0 + \frac{2A z_a z_b \mu^{1/2}}{1 + \alpha \beta \mu^{1/2}} \quad (8)$$

at  $\mu = 0$ ,  $A$  and  $\beta$  are constants ( $0.51 \text{ L}^{1/2} \text{ mol}^{-1/2}$  and  $3.29 \times 10^9 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ m}^{-1}$  at 25 °C, respectively),  $z_a$  and  $z_b$  are the effective charges on the two reactants, and  $\alpha$  is the effective size parameter. According to eq 8, a plot of  $\log k$  vs  $\mu^{1/2}/(1 + \alpha \beta \mu^{1/2})$  should be linear with a slope that represents the product of the effective charges on the reactants.

Although the equation is approximated only at ionic strengths much lower than those employed in this study and is strictly valid only in the limit as  $\mu \rightarrow 0$ , it is still instructive to see the result of its application. The size parameter,  $\alpha$ , was evaluated by taking the average of the radii for the reactant cation/anion contact pairs for each anion, i.e.,  $\alpha = (r_c + r_a)/2$ . The radii of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  were estimated to be 7.0 and 3.3 Å, respectively, from CPK space-filling models, using  $r = [(d_x d_y d_z)^{1/3}]/2$ . The hydrated radii of the anions, given in Table 1,<sup>17</sup> were used in the calculation of  $\alpha$ ; it should be noted that the slopes of the Debye–Hückel plots are not very sensitive to that value. Although reasonably linear plots are obtained, the

TABLE 1: Properties of the Anions

anion	hydrated radius, <sup>a</sup> Å	crystal ionic radius, <sup>a,b</sup> Å	pK <sub>a</sub> (conjugate acid) <sup>c</sup>	ΔG <sub>hyd</sub> <sup>d</sup> kJ/mol (at 298 K)
ClO <sub>4</sub> <sup>-</sup>	3.5	2.9	-4.8	-1270
SO <sub>4</sub> <sup>2-</sup>	4.0	2.9	2.0	-3202
HPO <sub>4</sub> <sup>2-</sup>	4.0	2.6	7.2	
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	4.0	2.6	2.2	-1594
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	4.5	1.8	4.8	-1460
F <sup>-</sup>	3.5	1.3	3.2	-1528
Cl <sup>-</sup>	3.0	1.8	-6.1	-1403
Br <sup>-</sup>	3.0	2.0	-9.0	-1377
I <sup>-</sup>	3.0	2.2	-9.5	-1339

<sup>a</sup> Reference 17. <sup>b</sup> Calculated from CPK space-filling models; see: Horvath, A. L. *Handbook of Aqueous Electrolyte Solutions*; Wiley: New York, 1985; p 344. <sup>c</sup> Reference 17. <sup>d</sup> Reference 28.

slopes for the quenching reaction (charge product = +4) are significantly less in the presence of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (+0.9) than for ClO<sub>4</sub><sup>-</sup> (+4.6). The effective charges for the recombination reaction decrease in the same order as dose  $k_q$ : ClO<sub>4</sub><sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Inasmuch as H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> have similar sizes and the same charge, the dependence on  $\mu$  should be the same if the observed salt effects are due only to the charge and size of the anion in the collisional domain. Clearly, as to be expected, a model based solely on the variation of the ionic strength of the solution cannot account for the observed results.

**B. Ion Pairing.** There can be no question but that the reactant cations are ion-paired with the dominant anions under the conditions of the experiments. The values of the equilibrium constants ( $K_{ip}$ ) for the 1:1 pairing of the reactant cations with the various anions (see supporting information) were calculated for solutions of  $\mu = 0.05$ – $0.8$  M through the use of the Fuoss equations (9) and (10),<sup>18</sup> where  $k$  is Boltzmann's constant,  $N$  is

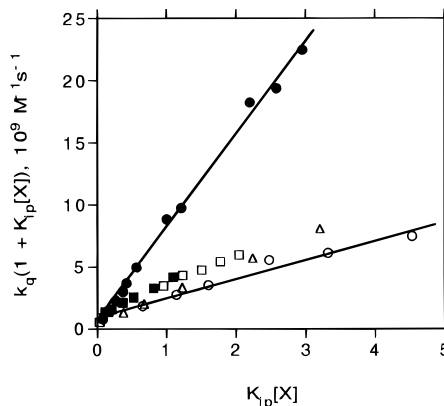
$$K_{ip} = \frac{4\pi N \sigma^3}{3000} \exp[-w(\sigma)/kT] \quad (9)$$

$$w(\sigma) = \frac{z_c z_a e^2}{\epsilon \sigma (1 + \beta \sigma \mu^{1/2})} \quad (10)$$

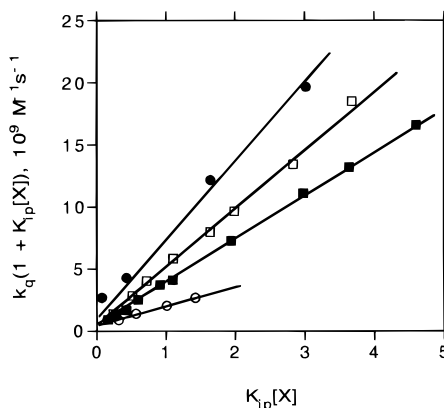
$$\epsilon = \epsilon_w + 2\delta^* c \quad (11)$$

Avogadro's number,  $\epsilon$  is the static dielectric constant of the solution, and  $\sigma$  is the distance of closest approach of anion and cation in the ion pair, which is given by the sum of the radii of the two species. Inasmuch as the addition of salts to the solvent decreases the static dielectric constant, values of  $\epsilon$  were calculated for each salt concentration by use of eq 11, where  $\epsilon_w$  is the dielectric constant of pure water,  $\delta^*$  is the average of the molar dielectric constant depression coefficients of the cations and anions of the electrolyte at 25 °C, and  $c$  is the molar concentration of the salt. The static dielectric constant decreases with increasing with temperature, but  $\delta^*$  varies <8% over the temperature range studied.<sup>19</sup>

The values of  $K_{ip}$  for \*Ru(bpy)<sub>3</sub><sup>2+</sup> and MV<sup>2+</sup> with the univalent anions are ~6 and ~3 M<sup>-1</sup>, respectively, at  $\mu = 0.1$  M and 25 °C; for both reactants,  $K_{ip} \sim 11$  M<sup>-1</sup> with the divalent anions. In the case of Ru(bpy)<sub>3</sub><sup>3+</sup> and MV<sup>•+</sup>,  $K_{ip} \sim 8$  and 2 M<sup>-1</sup>, respectively; for the univalent anions; for the divalent anions,  $K_{ip} \sim 25$  and 3 M<sup>-1</sup>, respectively. Thus, under the conditions of the experiments, \*Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(bpy)<sub>3</sub><sup>3+</sup> are largely ion-paired with at least one anion; the methylviologen species are less, but still significantly, ion-paired. As expected, the extent of ion pairing is somewhat greater for the divalent anions. However, there is nothing unusual about these numbers



**Figure 5.** Olson-Simonson treatment of quenching data for Na<sup>+</sup> salts of oxyanions at 25 °C: NaClO<sub>4</sub> (●), Na<sub>2</sub>SO<sub>4</sub> (□), Na<sub>2</sub>HPO<sub>4</sub> (■), NaH<sub>2</sub>PO<sub>4</sub> (○), Na(CH<sub>3</sub>CO<sub>2</sub>) (△). Lines are drawn only through the NaClO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> points for clarity.



**Figure 6.** Olson-Simonson treatment of quenching data for Na<sup>+</sup> salts of halide anions at 25 °C: NaF (○), NaCl (■), NaBr (□), NaI (●).

to account for the effect of the specific anions on  $k_q$  or  $k_{rec}$  and their activation parameters.

**C. Olson-Simonson Treatment.** The approach here is to consider the overall rate constant of the reaction between cations 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 ( $k_{nip}$ ).<sup>5</sup> Equation 12 relates these quantities, where  $[X]$  is the concentration of the dominant anion and  $K_{ip}$  is the ion-pairing equilibrium constant from above.

$$k_q = \frac{k_{nip}}{1 + K_{ip}[X]} + \frac{k_{ip}K_{ip}[X]}{1 + K_{ip}[X]} \quad (12)$$

Rearrangement of eq 12 leads to the prediction that a plot of  $k_q(1 + K_{ip}[X])$  vs  $K_{ip}[X]$  should be linear with slope =  $k_{ip}$  and intercept =  $k_{nip}$ . Inasmuch as  $K_{ip}$  can be calculated for each  $[X]$  as a function of temperature from eqs 9 and 10, all the information is known for the evaluation of  $k_{ip}$  and  $k_{nip}$ .

**(1) Quenching.** It turns out that the use of  $K_{ip}$  for either \*Ru(bpy)<sub>3</sub><sup>2+</sup> or MV<sup>2+</sup> in eq 12 has very little effect on the plots of the data. Figures 5 and 6 show the results at 25 °C for the oxyanions and halides, respectively, using  $K_{ip}$  for \*Ru(bpy)<sub>3</sub><sup>2+</sup>. The linear plots for all the electrolytes at 10, 25, 35, 45, and 60 °C all converge to intercepts of  $4.0 \times 10^8$ ,  $5.3 \times 10^8$ ,  $6.3 \times 10^8$ ,  $7.6 \times 10^8$ , and  $8.7 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>, respectively, values that represent  $k_{nip}$ . The slopes, which represent the quenching rate constants for the ion-paired species,  $k_{ip}$ , are given in Table 2 as a function of temperature. In general, the values of  $k_{ip}$  among the Na<sup>+</sup> salts diminish in the following order: ClO<sub>4</sub><sup>-</sup> > I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > HPO<sub>4</sub><sup>2-</sup> > CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > F<sup>-</sup>.

**TABLE 2: Values of  $k_{ip}$  for Quenching from the Olson–Simonson Treatment**

salt	$T, ^\circ\text{C}$	$k_{ip}, 10^9 \text{ M}^{-1} \text{ s}^{-1}$				
		10.0	25.0	35.0	45.0	60.0
NaClO <sub>4</sub>	5.8		7.6	8.7	9.5	12
Na <sub>2</sub> SO <sub>4</sub>	1.9		2.6	3.4	4.0	5.0
Na <sub>2</sub> HPO <sub>4</sub>	1.6		2.8	3.2	3.6	4.4
NaH <sub>2</sub> PO <sub>4</sub>	1.4		1.5	2.8	2.9	3.3
Na(CH <sub>3</sub> CO <sub>2</sub> )	1.5		2.4	2.6	3.5	4.0
NaF	1.2		1.6	2.0	2.0	3.9
NaCl	2.2		3.6	3.8	4.3	5.2
NaBr	2.3		4.8	4.9	5.7	6.8
NaI	4.1		5.9	7.0	8.0	9.5

**TABLE 3: Values of  $\Delta H^\ddagger$  and the Reorganization Energy ( $\lambda$ ) for the Quenching Reaction between Ion-Paired Species**

salt	$\Delta H^\ddagger, \text{kJ/mol}$	$\lambda, \text{eV}$
NaClO <sub>4</sub>	8.5	1.2
Na <sub>2</sub> SO <sub>4</sub>	12.9	1.4
Na <sub>2</sub> HPO <sub>4</sub>	12.7	1.4
NaH <sub>2</sub> PO <sub>4</sub>	12.7	1.4
Na(CH <sub>3</sub> CO <sub>2</sub> )	12.9	1.4
NaF	14.4	1.5
NaCl	10.2	1.3
NaBr	13.3	1.4
NaI	10.6	1.3

**(2) Charge Recombination.** A similar treatment of  $k_{rec}$  as a function of [salt], which is available only at 25 °C, for NaClO<sub>4</sub>, Na(CH<sub>3</sub>CO<sub>2</sub>), Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and NaH<sub>2</sub>PO<sub>4</sub> gives values of  $k_{ip}$  of  $1.8 \times 10^{10}$ ,  $1.1 \times 10^{10}$ ,  $9.2 \times 10^9$ ,  $7.4 \times 10^9$ , and  $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively; the values of  $k_{nip}$  are on the order of  $(1-2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The dependences of  $k_{ip}$  and  $k_{nip}$  on temperature for charge recombination were not evaluated due to the lower precision of the values of  $k_{rec}$ .

**D. Electron Transfer.** The calculated values of  $k_{ip}$  for quenching and charge recombination are independent of the concentration of the electrolyte and, thus, ionic strength. In a sense, the quantities that affect the rate of diffusion and encounter (radii,  $\mu$ ) have already been introduced in the calculation of  $K_{ip}$ , leaving  $k_{ip}$  to reflect the actual electron-transfer component of the overall reaction for the ion-paired reactants.

Inasmuch as  $k_{ip}$  for quenching is known as a function of temperature, it is possible to evaluate  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  through the application of the Eyring treatment.<sup>20</sup> Despite the long extrapolation of the plots of  $\ln(k_{ip}/T)$  vs  $1/T$  to the y axis,  $\Delta S^\ddagger$  for all nine electrolytes has an average value of  $-24 (\pm 4, \text{std dev}) \text{ J/(K}\cdot\text{mol)}$ , indicating that the variations in the electron-transfer rate constants of the ion-paired reactants are due mainly to differences in  $\Delta H^\ddagger$  (Table 3). Although the range of  $\Delta H^\ddagger$  is not large, one can see that the enthalpic barrier to electron transfer is lowest for NaClO<sub>4</sub> among the oxanions and is lowest for NaI and highest for NaF among the halides. Inasmuch as the effect of the electrolytes on  $k_{ip}$  for charge recombination is virtually the same as for quenching, it is likely that  $\Delta H^\ddagger$  follows the same pattern in that case as well.

It is clear that the various electrolytes, through ion pairing with the reactants, alter the energy barrier for electron transfer; at the same time, it is difficult to see how the electronic structure of the individual anions can mediate the transfer of an electron from a  $\pi^*$  orbital of a ligand of the excited photosensitizer into the  $\pi^*$  orbital of MV<sup>2+</sup> in the case of quenching and from the  $\pi^*$  orbital of MV<sup>•+</sup> into the hole in the  $t_{2g}$  orbital of Ru(bpy)<sub>3</sub><sup>3+</sup> in the case of charge recombination.

In the classical formulation of the Marcus theory of electron transfer, the rate constant is a function of the extent of electronic coupling between the donor and the acceptor, the reorganization

energy ( $\lambda$ ), and  $\Delta G^\ddagger$ , which is related by eq 13 to  $\lambda$  and  $\Delta G^\circ$ ,

$$\Delta G^\ddagger = \frac{(\Delta G^\circ + \lambda)^2}{4\lambda} \quad (13)$$

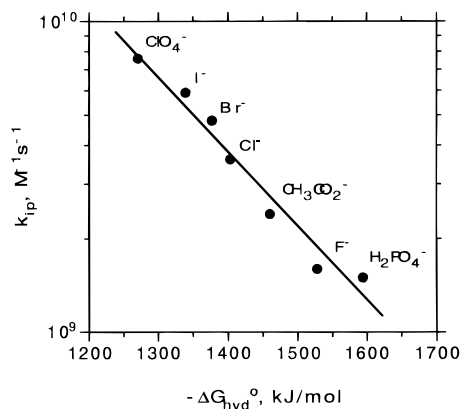
the reaction free energy.<sup>21</sup> Inasmuch as  $\Delta G^\circ$  is determined by the potentials of the reacting species, it should be noted that  $E^\circ$  could be different for the different supporting electrolytes due to variations in  $K_{ip}$  and the degree of ion pairing. However, the  $K_{ip}$ 's for all the univalent anions are virtually the same, and our experiments with the 1:1 electrolytes show that  $E^\circ$  is essentially invariant. Thus, because  $\Delta G^\circ$  is invariant ( $-0.42 \text{ eV}$  for quenching)<sup>22</sup> and the electronic coupling is likely to be the same for all the added electrolytes, the observed effects cannot be attributed to differences in the driving force of the reaction.

The reorganization energy is a measure of the free energy required to activate the motions of all the atoms of the initial state, including those in the solvent shell, from their equilibrium positions to those of the final state. The value of  $\lambda$  has two contributions:  $\lambda_{in}$  from the motion of the atoms of the reactants, which is insignificant for the species under consideration here, and  $\lambda_{out}$  from the reorganization of the solvent molecules and the ions that surround the reacting species in the solvent cage. The contribution to  $\lambda_{out}$  from the reorganization of the large number of dipolar solvent molecules that make up the cage ( $\lambda_{cage}$ ) will, undoubtedly, be larger than that from the reorganization of the smaller number of ions ( $\lambda_{ion}$ ) and their associated hydration spheres ( $\lambda_{hyd}$ ).<sup>6c,24</sup> Values of  $\lambda$  for the quenching reaction can be calculated from the slopes of plots of  $\ln(k_{ip}T^{1/2})$  vs  $1/T$  for the electrolytes;<sup>25</sup> a demonstration of the effect of ion pairing on  $\lambda$  for quenching is shown in Table 3, where  $\lambda$  covers a range between 1.2 eV for ClO<sub>4</sub><sup>−</sup> and 1.5 eV for F<sup>−</sup>.<sup>26</sup> Values of  $V$ , the electronic coupling coefficient, which can be extracted from the intercepts of these plots, show no observable variation with the different anions.

Because  $k_{nip}$  for quenching, which represents the electron-transfer reaction between non-ion-paired entities, is known as a function of temperature, it is possible to extract  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\lambda$  in a similar manner; the values are 10 kJ/mol,  $-45 \text{ J/(K}\cdot\text{mol)}$ , and 1.3 eV, respectively. Although the values of  $\Delta H^\ddagger$  and  $\lambda$  are within the lower end of the range for  $k_{ip}$ , it is striking that  $\Delta S^\ddagger$  is significantly more negative.

**E. Model.** The quenching or charge recombination solvent cage can be visualized in its simplest form as consisting of the donor and acceptor cations surrounded by the pairing anions, with the polar solvent, interspersed around and between the charged species, blending into the bulk; Na<sup>+</sup>, which is undoubtedly ion-paired with the anions, would not be expected to be associated in any way with the reactant cations. The transfer of an electron from the donor to the acceptor within the solvent cage, with a concomitant change in charge distribution, would result in the reorganization of the closely paired anions and their hydration spheres, as well as the solvent of the cage.

What role do the anions play in the control of the rate of electron transfer? One view is to consider them as spacers between the reacting cations; smaller anions would increase the rate by "tethering" the reactants more closely together, decreasing the distance over which electron transfer occurs, and enhancing the coupling between the reactants. However, there is no obvious correlation of  $k_{ip}$  with the hydrated radii of the anions nor their basicities (Table 1). Furthermore, the values of  $V$  that are obtained from the intercepts of the plots of  $\ln(k_{ip}T^{1/2})$  vs  $1/T$  show no discernible variation among the anions. We do not believe that this view is sufficient to account for the observed behavior of the system.



**Figure 7.** Correlation between  $k_{ip}$  for quenching at 25 °C and  $\Delta G_{hyd}^0$  of the univalent anions.

Inasmuch as the electronic coupling between the donor and the acceptor does not appear to be a function of the nature of the anion, attention should be directed to  $\lambda$  and the strength of the hydration spheres. Although  $\lambda_{cage}$  and  $\lambda_{ion}$  might be sensitive to the nature of the electrolyte, it is more likely that  $\lambda_{hyd}$ , reflecting the free energy involved in the solvation/desolvation processes, would be anion-specific.

We propose that the predominant free-energy term that governs the rate of electron transfer between the same cationic species in the same solvent at the same temperature is the standard free energy of hydration ( $\Delta G_{hyd}^0$ ) of the dominant anion;  $\Delta G_{hyd}^0$  refers to the reaction in which a gas-phase ion is brought into solution.  $\Delta G_{hyd}^0$ , of course, contains  $\Delta H_{hyd}^0$  the energy involved in changing the hydration sphere, and  $\Delta S_{hyd}^0$ ; this latter term is the sum of entropy terms involving electrostatics, volume, charge, the immobilization of the solvent molecules, and  $\Delta S_{struct}$ , the entropy change involved in the making and breaking of the water structure surrounding the anions.<sup>28</sup> If this hypothesis were true, there should be a quantitative correlation between  $k_{ip}$  (and those energy quantities that are derived therefrom, *i.e.*,  $\Delta H^\ddagger$  and  $\lambda$ ) and  $\Delta G_{hyd}^0$  (Table 1). Reasonably linear relationships exist between  $\Delta H^\ddagger$  or  $\lambda$  and  $\Delta G_{hyd}^0$ ; most importantly, however, Figure 7 shows a very satisfactory linear relationship between  $\log k_{ip}$  and  $\Delta G_{hyd}^0$  of the univalent anions at a constant temperature, with  $k_{ip}$  increasing as  $\Delta G_{hyd}^0$  becomes less negative. The divalent anions, even if the  $\Delta G_{hyd}^0$  data were available, cannot be compared directly with the univalent anions; their higher charge will affect differently the many factors that determine  $\lambda_{out}$ , including the specific structure of the anions around the reactants and the reorganization of the solvent of the cage.

Perchlorate ion, having the least negative  $\Delta G_{hyd}^0$ , is a very powerful breaker of the water structure and is able to reorganize its hydration sphere with the least cost in energy, making it the most hydrophobic of the anions. As a result,  $\text{ClO}_4^-$  makes the smallest contribution to the overall  $\lambda$  of the system and enhances the rate of electron transfer relative to the other anions. In truth,  $\text{ClO}_4^-$  does not accelerate the rate; it retards it to a lesser extent.

The values of  $\Delta H^\ddagger$  and  $\lambda$  that are derived from  $k_{nip}$  are approximately the same as those exhibited by  $\text{ClO}_4^-$  and  $\text{I}^-$ , anions that have the least negative values of  $\Delta G_{hyd}^0$  and the highest degree of hydrophobicity. Most importantly, the value of  $\Delta S^\ddagger$  for the non-ion-paired species is much more negative than those from  $k_{ip}$ , indicating that the process of electron transfer involves a much larger degree of microscopic order than when ions and their hydration spheres are involved.

**Back Electron Transfer.** Inasmuch as  $\eta_{ce} = k_{ce}/(k_{ce} + k_{bt})$  and  $\eta_{ce}^{-1} - 1 = k_{bt}/k_{ce}$ ,  $k_{bt}$  can be easily obtained from the values of  $k_{ce}$  that are calculated from the Eigen equation (14)

for the diffusion apart into bulk solution of two species that are initially in a solvent cage; the terms  $w(r, \mu)$  and  $\beta$  are given by eqs 15 and 16,<sup>29</sup> with  $w(a, \mu)$  equaling  $w(r, \mu)$  where  $r = a$ . Here,

$$k_{ce} = \frac{kT}{2\pi\eta a^2} \left( \frac{1}{r_B} + \frac{1}{r_A} \right) \frac{\exp[w(a, \mu)/kT]}{a \int_a^\infty r^{-2} \exp[w(r, \mu)/kT] dr} \quad (14)$$

$$w(r, \mu) = \frac{z_A z_B e^2}{2\epsilon r} \left( \frac{\exp(\beta \sigma_A \sqrt{\mu})}{1 + \beta \sigma_A \sqrt{\mu}} + \frac{\exp(\beta \sigma_B \sqrt{\mu})}{1 + \beta \sigma_B \sqrt{\mu}} \right) \exp(-\beta r \sqrt{\mu}) \quad (15)$$

$$\beta = \left( \frac{8\pi N e^2}{1000 \epsilon kT} \right)^{1/2} \quad (16)$$

$r_A$  and  $r_B$  are the radii of the reactants,  $a = r_A + r_B$ , and  $r$  is the distance separating the two reactants. The values of  $r_A$  and  $r_B$ ,  $\epsilon$ , and the hydrated ionic radii are the same as in the ion-pairing treatment above. The use of the following symbols is also the same:  $k$ ,  $N$ ,  $z_A$  and  $z_B$ , and  $\sigma$ ;  $e$  is the electronic charge, and  $\eta$  is the viscosity of the bulk solution. Inasmuch as the addition of salts increases the viscosity of the solution, values of  $\eta$  were taken from the literature tabulations as a function of [salt] and temperature.<sup>30</sup> Values of  $k_{ce}$  are given in the supporting information;  $E_a = 19.3$  kJ/mol for all the salts for cage escape.

For a given electrolyte,  $k_{bt}$  is independent of [salt] but is, of course, a function of temperature (supporting information); values of  $k_{bt}$  at the same temperature are in the following order:  $\text{ClO}_4^- \sim \text{I}^- > \text{Br}^- > \text{Cl}^- \sim \text{F}^- > \text{H}_2\text{PO}_4^- \sim \text{SO}_4^{2-} \sim \text{CH}_3\text{CO}_2^- \sim \text{HPO}_4^{2-}$ . Arrhenius plots yield very similar values of  $E_a$  ( $12 \pm 1$  kJ/mol) regardless of the supporting electrolyte; as would be expected for a system that consists of the same redox geminate pair and the same value of  $\Delta G_{bt}^0$  ( $-1.71$  eV).<sup>31</sup> As before, values of  $\lambda$  can be obtained from plots of  $\ln(k_{bt} T^{1/2})$  vs  $1/T$ ;  $\lambda \sim 1$  eV for all the anions; the electronic coupling constant is small ( $<0.05$  eV), as expected for solvent-separated ion pairs formed by diffusion.<sup>32</sup> Inasmuch as back electron transfer most likely lies in the inverted Marcus region, a higher value of  $\lambda$  results in a higher value of  $k_{bt}$  for the same  $\Delta G_{bt}^0$ .<sup>33</sup> Unfortunately, the range of values of  $k_{bt}$  is too small to show significant variations of  $\lambda$  over the relatively small temperature range available for study. In contrast, for the quenching reaction, which is undoubtedly in the normal Marcus region, the magnitude of the effect is larger; a higher value of  $\lambda$  results in a lower value of  $k_{ip}$ , as observed for  $\text{H}_2\text{PO}_4^-$  in comparison to  $\text{ClO}_4^-$ . The variation of  $\lambda$  with the dominant anion leads to the very interesting prediction that electron-transfer reactions between the same donor and acceptor in the presence of different supporting electrolytes may lie on different Marcus curves.

The model to account for the variations in  $k_{bt}$  is a simple extension of the one that was proposed above; it is reasonable to assume that the geminate redox species within the solvent cage, as with the species involved in the electron-transfer quenching, are ion-paired. The plot of  $\log k_{bt}$  vs  $\Delta G_{hyd}^0$  for the univalent anions is reasonably linear.

## Conclusions

Seemingly "innocent" anions in a polar medium can significantly affect the rates of intermolecular electron-transfer quenching and charge recombination reactions between cationic species and intramolecular back-electron-transfer reactions within the quenching solvent cage. The rate constants of electron transfer do not correlate with the hydrated size or basicity of the dominant anion. A quantitative model for

electron transfer is proposed that involves ion pairing between the cationic reactants and the dominant anion in bulk solution and within the electron-transfer complex. The reorganization of the anions and their hydration spheres contributes to  $\lambda$ ; the excellent correlation between the rate constants of the reactions and  $\Delta G^\circ_{\text{hyd}}$ , the standard free energy of hydration of the anions, shows that the rate of electron transfer is greatest when the dominant anion has the weakest-held hydration sphere and the strongest structure breaking ability in water. The variation in  $\lambda$  due to the anions could result in a family of Marcus curves, rather than one unique curve.

**Acknowledgment.** This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

**Supporting Information Available:** Tables listing the values of  $k_q$ ,  $k_{\text{rec}}$ , and  $\eta_{\text{ce}}$  as a function of electrolyte concentration and temperature; activation energies for  $k_q$  and  $k_{\text{rec}}$ ; values of  $K_{\text{ip}}$  as a function of electrolyte concentration and temperature; and values of  $k_{\text{ce}}$  and  $k_{\text{bt}}$  as a function of electrolyte concentration and temperature (19 pages). Ordering information is available on any current masthead page.

## References and Notes

- (1) (a) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177. (b) Bolletta, F.; Juris, A.; Maestri, M.; Sandrini, D. *Inorg. Chim. Acta* **1980**, *44*, L175. (c) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841. (d) Bolletta, F.; Maestri, M.; Balzani, V. *J. Phys. Chem.* **1976**, *80*, 2499.
- (2) Balzani, V.; Scandola, F. In *Energy Resources Through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic: New York, 1983; pp 1–48.
- (3) (a) Hoffman, M. Z.; Bolletta, F.; Moggi, L.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1989**, *18*, 219. (b) Buxton, G. V.; Mulazzani, Q. G.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 1055. (c) Clark, C. D.; Hoffman, M. Z. *Proc. Ind. Acad. Sci., (Chem. Sci.)*, in press.
- (4) Hoffman, M. Z. *J. Phys. Chem.* **1988**, *92*, 3458; **1991**, *95*, 2606.
- (5) Olson, A. R.; Simonson, T. R. *J. Chem. Phys.* **1949**, *17*, 1167.
- (6) (a) Piotrowiak, P.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 13052. (b) Lavallee, R. J.; Zimmt, M. B. *J. Phys. Chem.* **1994**, *98*, 4254. (c) Thompson, P. A.; Simon, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 5657. (d) Galán, M.; Jiménez, R.; Sánchez, F. *Ber. Bunsenges. Phys. Chem.* **1993**, *97*, 16. (e) Rampi Scandola, M. A.; Scandola, F.; Indelli, A. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2967. (f) Goede, W.; van Eldik, R. *Inorg. Chem.* **1994**, *33*, 2204.
- (7) Gaines, G. L. *J. Phys. Chem.* **1979**, *83*, 3089.
- (8) Kalyanasundaram, K.; Neumann-Spallart, M. *Chem. Phys. Lett.* **1982**, *88*, 7.
- (9) Ochiai, E. I.; Shaffer, D. I.; Wampler, D. L.; Schettler, P. D. *Transition Met. Chem.* **1986**, *11*, 241.
- (10) Chiorboli, C.; Indelli, M. T.; Rampi Scandola, M. A.; Scandola, F. *J. Phys. Chem.* **1988**, *92*, 156.
- (11) For a recent example, see: Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1994**, *98*, 11719.
- (12) Jones, G., II; Oh, C. *J. Phys. Chem.* **1994**, *98*, 2367.
- (13) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.
- (14) Yoshimura, A.; Sun, H.; Hoffman, M. Z. *J. Photochem. Photobiol. A: Chem.* **1993**, *70*, 29.
- (15) Sun, H.; Yoshimura, A.; Hoffman, M. Z. *J. Phys. Chem.* **1994**, *98*, 5058.
- (16) (a) Perlmuter-Hayman, B. *Prog. React. Kinet.* **1971**, *6*, 239. (b) Harned, H.; Owen, S. *The Physical Chemistry of Electrolyte Solutions*, 3rd ed.; Reinhold: New York, 1958; Chapter 2, p 3.
- (17) *Lange's Handbook of Chemistry*, 14th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1992.
- (18) Fuoss, R. M. *Trans. Faraday Soc.* **1934**, *30*, 967.
- (19) (a) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959. (b) Hasted, J. B.; Ritson, D. M.; Collie, C. H. *J. Chem. Phys.* **1948**, *16*, 1.
- (20) Baggot, J. E. In *Photoinduced Electron Transfer, Part B: Experimental Techniques and Medium Effects*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; Chapter 2.
- (21) Bolton, J. R.; Archer, M. D. *Adv. Chem. Ser.* **1991**, *228*, 7.
- (22) From  $\Delta G^\circ = E^\circ(\text{Ru}(\text{bpy})_3^{3+/2+}) - E^\circ(\text{MV}^{2+/+}) + w_p - w_r$ , where  $E^\circ(\text{Ru}(\text{bpy})_3^{3+/2+}) = -0.87 \text{ V}$ ,  $E^\circ(\text{MV}^{2+/+}) = -0.45 \text{ V}$  (vs NHE in  $\text{H}_2\text{O}$ ),  $w_p$  and  $w_r$  are the Coulombic work terms ( $\sim 10^{-2} \text{ eV}$ ).
- (23) (a) Lin, C. T.; Boettcher, M.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536. (b) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.
- (24) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Sidel, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748. (c) Blum, L. *J. Phys. Chem.* **1988**, *92*, 2969.
- (25) The following are some examples of the calculation of  $\lambda$  in this way: (a) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R.; Hubig, S.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786. (b) Yoshimura, A.; Nozaki, K.; Ikeda, N.; Ohno, T. *J. Am. Chem. Soc.* **1993**, *115*, 7521. (c) Finckh, P.; Heitele, H.; Volk, M.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1988**, *92*, 6584.
- (26) An estimate of  $\lambda_{\text{out}}$  can be made from Marcus theory:<sup>27</sup>  $\lambda_{\text{out}} = e^2((1/2r_a) + (1/2r_d) - (1/r_{\text{da}}))((1/n^2) - (1/\epsilon))$ , where  $r_a$  and  $r_d$  are the radii of the electron acceptor and donor, respectively,  $r_{\text{da}}$  is the distance between donor and acceptor, and  $n$  and  $\epsilon$  are the refractive index and the static dielectric constant of the medium, respectively.  $\lambda_{\text{out}}$  comes out to be on the order of 1 eV for  $\text{H}_2\text{O}$ .
- (27) Marcus, R. A. *J. Phys. Chem.* **1956**, *24*, 966; *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
- (28) (a) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985; Chapter 5. (b) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 233.
- (29) Melendard, G.; Eigen, M. *Z. Phys. Chem. (Munich)* **1954**, *1*, 176.
- (30) Stokes, R. H.; Mills, A. *Viscosity of Electrolytes and Related Properties*; Pergamon: Oxford, 1965.
- (31)  $E^\circ(\text{Ru}(\text{bpy})_3^{3+/2+}) = +1.26 \text{ eV}$  (vs NHE in  $\text{H}_2\text{O}$ ).<sup>23a</sup>
- (32) For example, see: Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
- (33) Suppan, P. *Top. Curr. Chem.* **1992**, *163*, 97.

JP953747Y