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Ion-pairing control of excited-state electron-transfer reactions
Effect of cations on cationic reactants

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Abstract

The rate constants for the oxidative quenching of *Ru(bpy)$_3^{2+}$ by MV^{2+} (k_q) and the cage escape yields (η_{ce}) of the redox products (Ru(bpy)$_3^{3+}$ and MV$^{\bullet+}$) were determined as a function of added electrolytes (Cl$^-$ salts of Li$^+$, Na$^+$, Cs$^+$, Ca^{2+}, La^{3+}) and temperature (10–60°C) in aqueous solution. At 25°C and constant [Cl$^-$], k_q is independent of the cation. There is, however, a specific cation effect on η_{ce} (La^{3+} > Ca^{2+} ~ Li$^+$ > Na$^+$ > Cs$^+$), which is attributed to differences in the rate constants of cage escape (k_{ce}) due to variations in the bulk properties of the solution (viscosity, dielectric constant); the rate constants of back electron transfer within the cage are essentially independent of the nature of the electrolyte cation. The reactant cations are extensively ion-paired by Cl$^-$ in bulk solution and within the quenching solvent cage. However, the electrolyte cations do not have any effect on the rates of electron transfer between the cationic species.

Keywords: Excited-state electron transfer; Ion-pairing; *Ru(bpy)$_3^{2+}$; MV^{2+}

1. Introduction

In a recent paper [1], we reported on the effect of anions (as their Na$^+$ salts) on the rate constant for the oxidative quenching (k_q) of *Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) by methylviologen (*N,N*′-dimethyl-2,2′-bipyridinium cation (MV^{2+})) and the cage escape yield (η_{ce}) of the redox products (Ru(bpy)$_3^{3+}$ and MV$^{\bullet+}$) into bulk aqueous solution. We found that at constant [anion], k_q is a function of the specific anion, decreasing in the order ClO$_4^-$ ≫ SO$_4^{2-}$ ~ HPO$_4^{2-}$ > H$_2$PO$_4^-$ ~ CH$_3$CO$_2^-$ and I$^-$ > Br$^-$ > Cl$^-$ > F$^-$. Because the cationic reactants are extensively ion-paired with the dominant anion, we concluded that the effect of the specific anions on the electron-transfer rate constants arose through variations in λ, the solvent reorganization energy, which were due to differences in the energetics of the hydration spheres of the anions and their abilities to break the surrounding water structure. We argued that the variations in η_{ce}, where the lowest values were shown for ClO$_4^-$, arose from the same specific anion effect on k_{bt}, the rate constant for back electron transfer within the quenching solvent cage.

Of course, the cations from the added electrolyte would ion-pair with the anions in the solution, but, due to electrostatics, would not be expected to interact directly with the reactant cations. Because the anions are also ion-paired to the reactant cations, the issue is whether these cation–anion–reactive cation interactions would have any influence on the rates of electron transfer within such electrostatically-assembled supramolecular entities. The results would be important for the understanding of the role of presumably 'innocent' spectator ions in electron transfer reactions in aqueous solution. In this study, values of k_q and η_{ce} were measured as a function of temperature (10–60°C) for the *Ru(bpy)$_3^{2+}$/MV^{2+} system in the presence of Li$^+$, Na$^+$, Cs$^+$, Ca^{2+}, and La^{3+} as their Cl$^-$ salts.

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2. Experimental details

[Ru(bpy)$_3$]Cl$_2$ (GFS Chemicals) was recrystallized from water and dried over silica gel. Methylviologen dichloride (Aldrich) was recrystallised several times from methanol and dried under vacuum for over 24 h. CaCl$_2$ (Baker Analyzed Reagent), NaCl (Johnson Matthey Chemicals, Puratronic), LaCl$_3$ (Aldrich), LiCl, and CsCl (Fluka) (all > 99.5% purity) were oven-dried at 150°C for more than 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 Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1}. The concentration of the supporting 1:1 electrolyte was 0.1 M.

Ground-state 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; a red filter was placed in front of the monochromator (Instruments SA) in the emission measurements and 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 ±0.1°C over the 10–60°C range.

All solutions were contained in 2 × 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. Quenching experiments were carried out on air-equilibrated or deaerated solutions ([Ru(bpy)$_3^{2+}$] = 45 μM); values of k_q with estimated errors of ±5% were obtained from slopes of the plots of the observed first-order rate constants for the decay of the emission from *Ru(bpy)$_3^{2+}$ (λ = 605 nm) as a function of [MV^{2+}] (0.5–10 mM) for four or five different quencher concentrations at each electrolyte concentration.

The quantum yield of redox products in bulk solution is a measure of the number of redox equivalents generated per photon absorbed; $\Phi = \Delta[\mathrm{MV}^{\bullet +}]/\Delta[\mathrm{Ru(bpy)}_3^{2+}]$. Δ[MV$^{\bullet+}$] and Δ[*Ru(bpy)$_3^{2+}$] were obtained through an application of Beer's law ($\Delta A = \epsilon_\lambda l \Delta[c]$) from ΔA at 605 nm (at 5–10 μs after the laser pulse) and 450 nm (at t = 0 for solutions containing only Ru(bpy)$_3^{2+}$ with the same absorbance at 532 nm as with quencher present), respectively; l = 2 cm, ϵ_{605} is the molar absorptivity of MV$^{\bullet+}$ at 605 nm (1.3 × 10^4 M^{-1} cm^{-1}) [2], and ϵ_{450} (−1.0 × 10^4 M^{-1} cm^{-1}) represents the difference in the ϵ-values of the excited and ground states of Ru(bpy)$_3^{2+}$ at 450 nm [3]. Values of η_{ce} (estimated error, ±7.5%) were calculated for solutions containing 45 μM Ru(bpy)$_3^{2+}$ and ≤ 5 mM MV^{2+} from the slopes of linear plots of Φ vs. η_q, or by averaging η_{ce} values obtained from three to five duplicate solutions with 2 mM MV^{2+}; η_q was calculated from $(k_{obs} - k_o)/k_{obs}$, where k_{obs} is the observed first-order rate constant for the decay of *Ru(bpy)$_3^{2+}$ in the presence of MV^{2+}.

3. 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 *Ru(bpy)$_3^{2+}$ in the absence of air and MV^{2+} ($\tau_o = 1/k_o$). At the concentrations of MV^{2+} used in this study, no change in its absorption spectrum was evident. Reversible potentials from the cyclic voltammetry experiments were +1.26 V for Ru(bpy)$^{3+/2+}$ and −0.45 V for MV$^{2+/\bullet+}$ vs. NHE, irrespective of the nature of the electrolyte at the concentrations employed in the photochemical studies; the observed small variations of 10–20 mV with the different electrolytes are within the experimental error.

Values of k_q and η_{ce} were obtained as a function of temperature and the concentration of added electrolyte. Fig. 1 shows the plot of k_q vs. [salt] for the Cl$^-$ salts of the cations at 25°C; the expected general increase in k_q toward a plateau value as [salt] is increased is clearly evident. The figure also shows that the variation of the cation results in small, but not negligible, changes in the values of the rate constants. Values of k_q at selected [salt] as a function of temperature are given in Table 1. As expected, k_q is a positive function of temperature; plots of log k_q vs. $1/T$ are linear for all added electrolytes with E_a = 13–14 kJ mol^{-1}, independent of the concentration of the electrolyte.

The values of η_{ce} decrease with increasing [salt] (Fig. 2) and increase with increasing temperature (Table 2). Despite the relative insensitivity of k_q to the nature of the cation of the Cl$^-$ salts, η_{ce} is clearly a function of the cation; η_{ce} is lowest when CsCl is the electrolyte and highest in the pres-

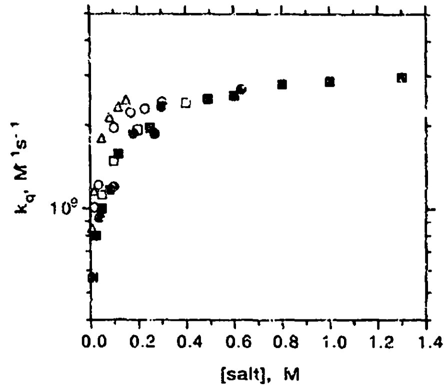

Fig. 1. Values of k_q as a function of [salt] at 25°C: LiCl (□), NaCl (■), CsCl (●), CaCl$_2$ (○), LaCl$_3$ (△).

Table 1
Values of k_q (in units of 10^9 M^{-1}s^{-1}) as a function of [salt] temperature

[salt] (M)	T (°C) 10.0	25.0	35.0	45.0	60.0
NaCl					
0.050	0.625	1.00	1.06	1.25	1.47
0.10	0.830	1.38	1.53	1.66	2.08
0.20	1.06	1.95	1.87	2.11	2.70
0.40	1.40		2.47	2.81	3.37
0.80	1.67	2.79	2.96	3.28	3.92
CsCl					
0.050	0.763	0.930	1.38	1.50	1.87
0.10	1.09	1.20	2.00	2.08	2.44
0.20	1.34	1.49	2.38	2.58	3.30
0.40	1.80		2.92	3.34	4.30
0.80	2.19		3.62	4.20	5.00
LiCl					
0.050	0.755	1.12	1.35	1.53	1.85
0.10	1.04	1.49	1.82	1.98	2.37
0.20	1.33	1.93	2.16	2.62	3.10
0.40	1.66	2.40	2.67	3.18	3.81
0.80	1.85		2.95	3.41	4.12
$LaCl_3$					
0.0083	0.699	0.850	1.11	1.32	1.44
0.017	0.921	1.16	1.52	1.79	2.01
0.033	1.14	1.48	1.94	2.25	2.53
0.067	1.55	1.96	2.37	2.87	3.28
0.13	1.81	2.39	2.78	3.49	3.68

	T (°C) 10.0	25.0	40.0	60.0
$CaCl_2$				
0.016	0.729	1.01	1.36	1.87
0.033	0.990	1.22	2.19	2.40
0.067	1.33		2.41	3.11
0.13	1.78	2.09	3.16	4.20
0.27	2.00	2.35	3.44	4.88

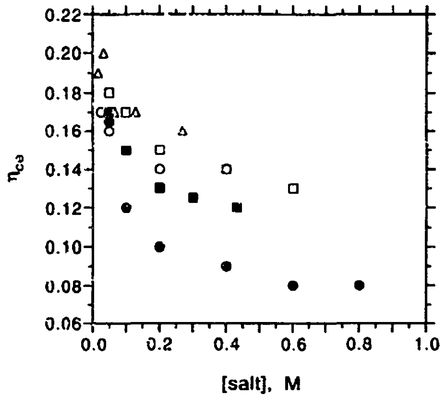

Fig. 2. Values of η_{ce} as a function of [salt] at 25°C: LiCl (□), NaCl (■), CsCl (●), $CaCl_2$ (○), $LaCl_3$ (△).

ence of LiCl and $LaCl_3$. For reference, the value of η_{ce} obtained at 25°C in the absence of any added electrolyte is 0.20.

Table 2
Values of η_{ce} as a function of [salt] and temperature

[salt] (M)	T (°C) 10.0	25.0	35.0	45.0	60.0
NaCl					
0.050		0.17	0.15	0.19	0.22
0.10	0.15	0.15	0.15	0.17	0.19
0.20	0.12	0.12	0.15	0.16	0.19
0.30		0.12			
0.40	0.11	0.12	0.14	0.16	0.18
CsCl					
0.050	0.16	0.17	0.17	0.20	0.20
0.10	0.13	0.12	0.15	0.18	0.17
0.20	0.13	0.10	0.16	0.20	0.19
0.40	0.11	0.090	0.14	0.18	0.17
0.60		0.080			
0.80	0.10	0.080	0.12	0.14	0.14
LiCl					
0.050	0.16	0.18	0.18	0.18	0.22
0.10	0.14	0.17	0.16	0.19	0.20
0.20	0.13	0.15	0.16	0.17	0.19
0.40	0.12	0.14	0.15	0.16	0.18
0.60		0.13			
0.80	0.11		0.13	0.14	0.15
$LaCl_3$					
0.0083	0.12	0.16	0.20	0.23	0.24
0.017	0.11	0.20	0.21	0.16	0.24
0.033	0.12	0.17	0.19	0.16	0.21
0.067	0.090	0.17	0.19	0.19	0.22
0.13	0.090	0.16	0.17	0.20	0.22

	T (°C) 25.0	40.0	60.0
$CaCl_2$			
0.017	0.17	0.19	0.22
0.033	0.16	0.17	0.20
0.067	0.15	0.17	0.19
0.13	0.14	0.16	0.18
0.27	0.14	0.13	0.15

4. Discussion

4.1. Mechanism

The mechanism of the quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+} has been studied in very great detail, and can be expressed by reactions (1)–(3).

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \tag{1}$$

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

$$^*Ru(bpy)_3^{2+} + MV^{2+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + MV^{\bullet+} \tag{3}$$

The quantum yield of the redox products released into solution (Φ) is given by the expression $\Phi = \eta_* \eta_q \eta_{ce}$, where η_* is the efficiency of formation of $^*Ru(bpy)_3^{2+}$ in the excitation process (~1) [4] and η_q is the efficiency of the quenching of the excited state ($\eta_q = k_q[MV^{2+}]/(k_q[MV^{2+}]+k_o)$). According to the conventional cage escape model [5], 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)). Therefore, $\eta_{ce} = k_{ce}/(k_{ce}+k_{bt})$ and $(\eta_{ce}^{-1}-1) = k_{bt}/k_{ce}$.

$$^*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow [Ru(bpy)_3^{3+} \cdots MV^{\bullet +}] \quad (4)$$

$$[Ru(bpy)_3^{3+} \cdots MV^{\bullet +}] \xrightarrow{k_{bt}} [Ru(bpy)_3^{2+} \cdots MV^{2+}] \quad (5)$$

$$[Ru(bpy)_3^{3+} \cdots MV^{\bullet +}] \xrightarrow{k_{ce}} Ru(bpy)_3^{3+} + MV^{\bullet +} \quad (6)$$

4.2. Quenching

Unlike the situation with the anions [1], the dependence of k_q as a function of [salt] is practically the same for the different cations (Fig. 1), although the data are not as superposable as one might expect given their very high degree of reproducibility and low intrinsic experimental error; in particular, the greatest deviations are shown for $CaCl_2$ and $LaCl_3$. It was pointed out many years ago by Olson and Simonson [6] in their study of the effect of the presence of 'inert' salts on the reaction rate between ions of the same charge, that variations in the rate constants are almost exclusively due to the concentration and nature of the oppositely-charged salt ions. When the data in Fig. 1 are replotted as a function of $[Cl^-]$, the coincidence of the points is very much improved (Fig. 3).

The Olson–Simonson treatment considers the overall rate constant of the reaction between cations to be 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}) [6]. Eq. (7) relates these quantities for the situation here; K_{ip} is the ion-pairing equilibrium constant.

$$k = \frac{k_{nip}}{1+K_{ip}[X]} + \frac{k_{ip}K_{ip}[X]}{1+K_{ip}[X]} \quad (7)$$

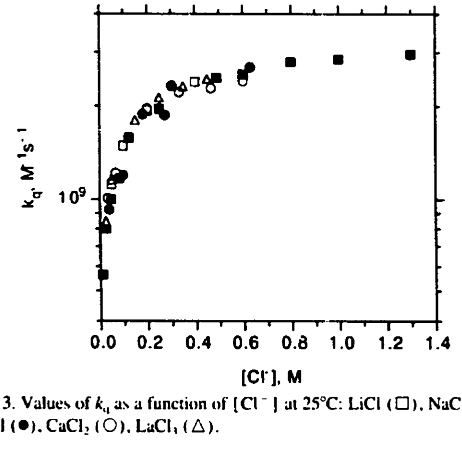

Fig. 3. Values of k_q as a function of $[Cl^-]$ at 25°C: LiCl (□), NaCl (■), CsCl (●), $CaCl_2$ (○), $LaCl_3$ (△).

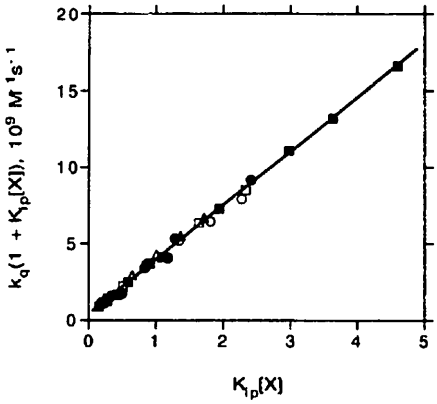

Fig. 4. Olson–Simonson treatment of k_q at 25°C: LiCl (□), NaCl (■), CsCl (●), $CaCl_2$ (○), $LaCl_3$ (△).

K_{ip} can be calculated for a 1:1 pair by means of the Fuoss equation [7]. As was shown earlier [1], K_{ip} for $^*Ru(bpy)_3^{2+}$ and MV^{2+} with Cl^- are ~6 and ~3 M^{-1}, respectively, at $\mu = 0.1$ M and 25°C; under the conditions of the experiments, $^*Ru(bpy)_3^{2+}$ is largely ion-paired with at least one Cl^-; MV^{2+} is less, but still significantly, ion-paired. Rearrangement of Eq. (7) leads to the prediction that a plot of $k(1+K_{ip}[Cl^-])$ vs. $K_{ip}[Cl^-]$ should be linear with slope k_{ip} and intercept k_{nip}.

Fig. 4 shows the Olson–Simonson plot for k_q at 25°C; it is clear that the nature of the electrolyte cation does not influence the ion-pairing between Cl^- and the reactant cations. The values of k_{ip} and k_{nip} from the slope and intercept of the plot are 3.5×10^9 M^{-1} s^{-1} and 4×10^8 M^{-1} s^{-1}, respectively; these values are virtually identical with those of k_{ip} for Cl^- and k_{nip} reported previously [1]. An Eyring treatment of the earlier data [1] yielded the same value of $\Delta H^{\ddagger}$ (10 kJ mol^{-1}) for k_{ip} and k_{nip}. The order of magnitude difference in those rate constants is attributed to the very large variation in $\Delta S^{\ddagger}$, which is −24 and −45 J K^{-1} mol^{-1} for k_{ip} and k_{nip}, respectively; it is clear that ion-pairing with Cl^- greatly raises the degree of disorder of the transition state in the electron transfer quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+}.

4.3. Back electron transfer

Values of k_{bt} can be obtained from the experimental values of η_{ce} and the calculated values of k_{ce} from the Eigen equation [8] for the diffusion into bulk solution of two species initially in the solvent cage. The important parameters that affect k_{ce} are the charges and radii of the reactants, the distance of closest approach of ion-paired anions and cations in the solvent cage, and the static dielectric constant (ϵ) and viscosity (η) of the bulk solution. For the diffusion of $Ru(bpy)_3^{3+}$ and $MV^{\bullet +}$ and ion-paired Cl^- out of the cage into bulk solution, all the terms in the Eigen equation are the same for all the electrolytes except ϵ and η. Values of ϵ were calculated for each salt concentration by use of Eq. (8), where ϵ_w is the dielectric constant of pure water, δ^* 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 value of ϵ decreases with increasing temperature, but δ^* varies $<8\%$ over the temperature range studied [9]. Values of η were taken from literature tabulations as a function of [salt] and temperature [10]. Calculated values of k_{ce} range between $\sim 4\times10^{9}$ and $\sim 1\times10^{10}$ s^{-1} at 10 and 60°C, respectively; E_a of k_{ce} for all the salts is 19.3 kJ mol^{-1}.

$$\epsilon=\epsilon_w+2\delta^* c \qquad (8)$$

The values of k_{bt} calculated from k_{ce} and η_{ce} are the same to $<5\%$ for all five Cl^- salts used, and are, of course, a function of temperature: $k_{bt}=2.4\times10^{10}$, 3.3×10^{10}, 4.0×10^{10}, 4.3×10^{10}, and 5.5×10^{10} M^{-1} s^{-1} at 10, 25, 35, 45, and 60°C, respectively, corresponding to an activation energy of 13 kJ mol^{-1}.

5. Conclusions

In summary, the differences in η_{ce} for the Cl^- salts originate from the values of k_{ce}, which are fairly sensitive to the variations in the solution viscosity and static dielectric constant; in contrast, k_q, which also has diffusional components, has a relatively weaker dependence on those solution medium parameters. The values of k_{ip}, which reflect the actual electron-transfer component of the quenching reaction [1], and k_{bt} are independent of the nature of the electrolyte cation. Despite the ion-pairing of the cationic reactants and the electrolyte cations with the dominant anion in the bulk solution and the electron-transfer solvent cage, the electrolyte cations do not affect the rates of electron-transfer between the cationic reactants in quenching or back electron transfer.

Acknowledgements

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