Solvent Reorganization Energies in Excited-State Electron-Transfer Reactions. Oxidative Quenching of the MLCT Excited States of Ru(II)-Diimine Complexes

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Introduction

According to the Marcus theory of electron transfer, the rate constant for intramolecular electron transfer (k_{et}) is controlled by the reaction free energy ($\Delta G°$) and the reorganization energy (λ); the latter quantity 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.[1] The value of λ has two contributions: λ_{in} from the motion of the atoms of the reactants, which is generally insignificant for substitution-inert metal complexes and radicals that have essentially the same structure as their parent molecules, and λ_{out} from the reorganization of the solvent molecules and the ions that surround the reacting species in the solvent cage.[2]

The well-known prediction of Marcus theory is that a plot of log k_{et} vs $\Delta G_{et}°$ for a group of species within an homologous series will describe a bell-shaped curve that defines the normal and inverted Marcus regions; at the maximum of the curve, $\lambda = -\Delta G_{et}°$. It is perfectly evident, but usually unstated, that the validity of the prediction depends on the constancy of the value of λ for the species examined. Recently, we showed that in the oxidative quenching of the luminescent MLCT excited state of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by methylviogen (1,1-dimethyl-4,4′-bipyridine dication; MV^{2+}) in aqueous solution, λ for forward ($^*Ru(bpy)_3^{2+} + MV^{2+}$) and reverse ($Ru(bpy)_3^{3+} + MV^{\bullet +}$) electron transfer was dependent on the hydration properties of the anion (but not the cation) of the supporting electrolyte;[3,4] in the reductive quenching of $^*Ru(bpy)_3^{2+}$ by aromatic amines in 1:1 (v/v) CH_3CN/H_2O solutions, λ for forward and reverse electron transfer was dependent on the structure and size of the quenchers and the nature of the ring substituents.[5,6] The results emphasized that differences in the solution medium and the structure and nature of the reactants can lead to different values of λ, resulting in data for an ostensibly homologous series that lie on different Marcus curves.

More recently, as part of our inquiry into whether the proposed delocalization of the transferred electron among the ligands in $^*Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline) (in contrast to the established electron localization in $^*Ru(bpy)_3^{2+}$ in fluid solution)[7] is of consequence to their photochemistry and photophysics, we reported that the quenching of both excited states by MV^{2+} had the same activation energy;[8] we concluded that since $\Delta G_{et}°$ is the same for both systems, λ must also be the same.

At issue is the generality of the effect of specific anions and the influence of electron-withdrawing and -donating ligand substituents on λ and the rate of electron transfer. In this study, we determined the rate constants (k_q) for the oxidative quenching of $^*Ru(phen)_3^{2+}$, $^*Ru(Clphen)_3^{2+}$ (Clphen = 5-chloro-1,10-phenanthroline), and $^*Ru(Me_2phen)_3^{2+}$ (Me_2phen = 5,6-dimethyl-1,10-phenanthroline) by MV^{2+} as a function of temperature in aqueous solution in the presence of the same concentration (0.1 M) of 1:1 supporting electrolytes ($NaClO_4$, NaH_2PO_4, NaF, NaCl, NaBr, NaI).[9] The values of k_{et} were calculated by use of the diffusional model; values of λ were evaluated from the dependence of k_{et} on T.

Experimental Section

$[Ru(phen)_3]Cl_2$, $[Ru(Me_2phen)_3]Cl_2$, and $[Ru(Clphen)_3]Cl_2$ were available from our laboratory stock; the compounds were recrystallized from water and dried over silica gel. Methyl viologen dichloride (Aldrich) was recrystallized several times from methanol, and dried under vacuum for more than 24 h. $NaClO_4$ and NaF (GFS Chemicals), NaH_2PO_4 (Baker Analyzed Reagent), NaCl (Johnson Matthey, Puratronic), and NaBr and NaI (Fluka) were all >99.5% purity, and these were dried in an oven 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.

Absorption spectra were measured with a diode array spectrophotometer (Hewlett-Packard 8452A); luminescence spectra were obtained with a Perkin-Elmer MPF2A spectrofluorimeter. Time-resolved emission measurements were made with a Nd:YAG laser (Quantel YG581), details of which have been described before;[10] the data were averaged for 10−20 shots. Temperatures of the solutions were controlled at 10−60 (±0.1) °C by a thermostated Brinkman Instruments RM6 water bath.

For the emission experiments, the solutions, which were deaerated by purging with Ar for 20 min, were contained in 2 × 1-cm cells, excited along the shorter path, and analyzed along the longer path. Quenching experiments were carried out on 45 μM RuL_3^{2+} solutions ($\mu = 0.1$ M with the appropriate salt). Values of k_q at each temperature were obtained from the slopes of linear plots of the observed first-order decay rate constant (k_{obs}) of the emission from $^*RuL_3^{2+}$ as a function of $[MV^{2+}\}$ for at least four different concentrations in the range 0.5−10 mM, and were reproducible with an error of <5%.

Results and Discussion

Quenching. The presence of the background electrolytes had no effect on the absorption or emission spectra of the complexes nor on their excited-state lifetimes in the absence of air; at the concentrations of MV^{2+} used, no changes in its absorption spectrum was evident. Values of k_q are given in Table 1.

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Table 1. Values of k_q (in Units of 10^9 M^{-1} s^{-1}) for the Reaction of $*RuL^{2+}$ with MV^{2+} in the Presence of 0.1 M Salts as a Function of Temperature

T, °C	NaH_2PO_4	NaF	NaCl	NaBr	NaI	$NaClO_4$
			$Ru(phen)_3^{2+}$			
10	0.94	0.87	1.2	1.7	2.1	2.9
20	1.2	1.1	1.5	1.9	2.6	3.9
30	1.5	1.4	1.8	2.3	3.1	4.5
40	1.8	1.5	2.2	2.7	3.7	5.1
50	2.2	1.7	2.5	3.1	4.0	6.5
60	2.6	1.8	2.8	3.6	4.7	6.9
			$Ru(Me_2phen)_3^{2+}$			
10	0.92	0.91	1.4	1.6		
20	1.1	1.1	1.7	1.9	2.9	
30	1.4	1.4	2.2	2.3	3.6	
40	1.7	1.8	2.6	2.7	4.1	
50	1.9	2.1	3.0	3.3	4.7	
60	2.4	2.4	3.4	3.8	5.6	
			$Ru(Clphen)_3^{2+}$			
10	0.77	0.71	1.1	1.4	2.3	
20	1.0	0.89	1.3	1.7	2.7	
30	1.2	1.1	1.6	2.0	3.1	
40	1.4	1.3	2.0	2.4	3.6	
50	1.7	1.6	2.5	2.6	4.1	
60	2.0	1.9	2.5	3.2	4.6	

The oxidative quenching of $*RuL_3^{2+}$ by MV^{2+} can be described by reactions 1−3.

$$RuL_3^{2+} \xrightarrow{h\nu} *RuL_3^{2+} \tag{1}$$

$$*RuL_3^{2+} \xrightarrow{k_o} RuL_3^{2+} + h\nu' \tag{2}$$

$$*RuL_3^{2+} + MV^{2+} \xrightarrow{k_q} RuL_3^{3+} + MV^{\bullet +} \tag{3}$$

In its simplest model,[11] electron-transfer quenching between $*RuL_3^{2+}$ and MV^{2+} can be represented by the diffusional formation of a precursor complex (reaction 4), followed by the diffusional breakup of the complex (reverse of reaction 4) in competition with the electron-transfer step (reaction 5). Because RuL_3^{3+} and $MV^{\bullet +}$ are high energy species, the reverse of reaction 5 is highly endoergic, making that reaction very slow compared to subsequent steps.

$$*RuL_3^{2+} + MV^{2+} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [*RuL_3^{2+}\cdots MV^{2+}] \tag{4}$$

$$[*RuL_3^{2+}\cdots MV^{2+}] \xrightarrow{k_{et}} [RuL_3^{3+}\cdots MV^{\bullet +}] \tag{5}$$

A steady-state treatment of reactions 4 and 5 yields eq 6, where $K_d = k_d/k_{-d}$.

$$\frac{1}{k_q} - \frac{1}{k_d} = \frac{1}{K_d k_{et}} \tag{6}$$

Electron Transfer. Values of k_d and k_{-d} (see Supporting Information) were calculated from the Debye−Smoluchowski[12,13] and Eigen[14] equations, respectively, as has been done before,[15] by taking molecular and ionic radii from CPK models (RuL_3^{2+}, 7.5 Å for phen and Clphen, 7.6 Å for Me_2phen; MV^{2+}, 3.3 Å) and the literature.[16] The principle effect of temperature in these equations is the direct statement of that parameter and the variations in solution viscosity (η) and dielectric constant (ϵ); values of η were taken from literature tabulations as a function of [salt] and temperature[17] and ϵ was calculated as done previously[3] from knowledge of the molar dielectric constant depression coeffiecients of the cations and anions of the electrolytes.[18] Values of k_{et} as a function of temperature calculated with this model are also given in the Supporting Information.

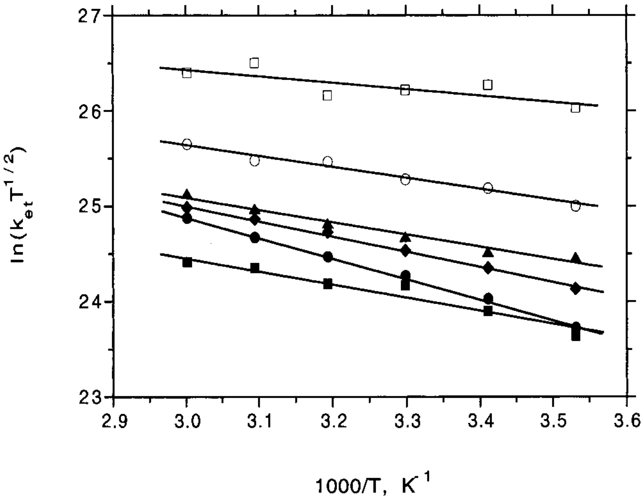

Figure 1. Plot of $\ln(k_{et}T^{1/2})$ vs $1/T$ for the quenching of $*Ru(phen)_3^{2+}$ by MV^{2+} in the presence of 0.1 M $NaClO_4$ (□), NaI (○), NaBr (▲), NaCl (◆), NaF (■), and NaH_2PO_4 (●).

Reorganization Energy. In the semiclassical formulation of Marcus theory, k_{et} is given by eq 7, where *V* is the electronic coupling coefficient, and *h* and *k* are Planck's and Boltzmann's constants, respectively; values of λ and *V* can be determined from the slopes and intercepts of linear plots of $\ln(k_{et}T^{1/2})$ vs $1/T$.[19−21]

$$k_{et} = \frac{4\pi^2 V^2}{h(4\pi\lambda kT)^{1/2}} \exp\left[\frac{-(\lambda + \Delta G_{et}^\circ)^2}{4\lambda kT}\right] \tag{7}$$

An example of this graphical treatment is shown in Figure 1 for the quenching of $*Ru(phen)_3^{2+}$ by MV^{2+}, where λ_{in} is insignificant so that $\lambda \approx \lambda_{out}$, in the presence of 0.1 M $H_2PO_4^-$, F^-, Cl^-, Br^-, I^-, and ClO_4^- (as their Na^+ salts). The values of λ for this reaction, which are estimated to have errors of ±10%, are evaluated from the plots by using ΔG_{et}° (Table 2); they range between 0.89 eV for $NaClO_4$ and 1.5 eV for NaH_2PO_4 (Table 3). We had argued earlier[3] that the predominant free-energy term that governs the rate of electron transfer

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Table 2. Energy Parameters for the Quenching of $^{*}RuL_3^{2+}$ by MV^{2+}

complex	$E°(RuL_3^{3+/2+})$, V (vs NHE in H_2O)[a]	E_{oo}, eV [a]	$\Delta G_{et}°$, eV [b]
$Ru(bpy)_3^{2+}$	1.26	2.12	−0.41
$Ru(phen)_3^{2+}$	1.26	2.13	−0.42
$Ru(Me_2phen)_3^{2+}$	1.20	2.13	−0.48
$Ru(Clphen)_3^{2+}$	1.36	2.13	−0.32

[a] Reference 26. [b] From $\Delta G_{et}° = E°(RuL_3^{3+/2+}) - E°(MV^{2+/+}) - E_{oo} + w_p - w_r$; $E°(MV^{2+/+}) = -0.45$ V vs NHE in H_2O (ref 27); w_p and w_r are Coulombic work terms (~0.01 eV). The values of $\Delta G_{et}°$ can be taken to be independent of temperature inasmuch as $(\partial E°/\partial T)_p = \Delta S°/nF$ and $\Delta S°$ is very small for this electron-transfer reaction within the quenching cage where λ_{in} is not significant.

Table 3. Values of λ (eV) for RuL_3^{2+} in the Presence of Salts ($\mu = 0.1$ M)

salt ($\Delta G_{hyd}°$, kJ mol^{-1})[a]	phen	Me_2phen	Clphen
$NaClO_4$ (−1270)	0.89		
NaI (−1339)	1.1	1.1	0.81
NaBr (−1377)	1.2	1.4	1.0
NaCl (−1403)	1.3	1.4	1.2
NaF (−1528)	1.2	1.5	1.3
NaH_2PO_4 (−1594)	1.5	1.5	1.3

[a] Reference 22.

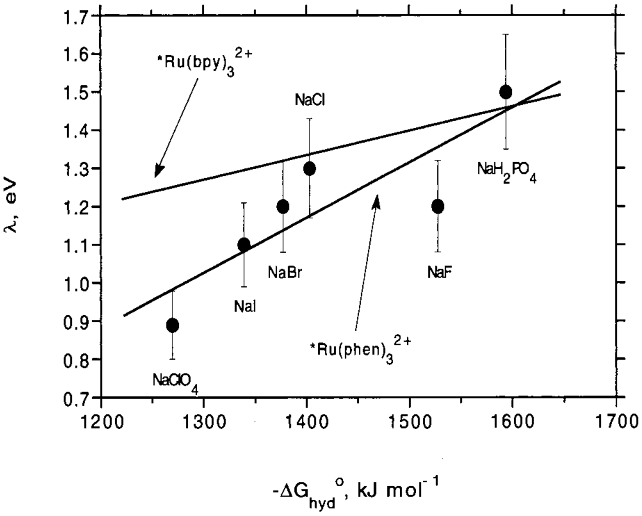

Figure 2. Plot of λ vs $-\Delta G_{hyd}°$ for the quenching of $^{*}Ru(phen)_3^{2+}$ by MV^{2+} in the presence of supporting electrolytes (points and lower line). Upper line is from the data in ref 3 for the quenching of $^{*}Ru(bpy)_3^{2+}$.

between the same cationic species in the same solvent at the same temperature is the standard free energy of hydration ($\Delta G_{hyd}°$) of the dominant anion, which reflects the hydration enthalpies and the structure-making/breaking characteristics of the anions;[22] we had also shown that values of V show no observable variation with the different anions. The correlation between λ and $\Delta G_{hyd}°$ is reasonably linear (Figure 2) and shows that those anions that are able to reorganize their hydration spheres without having to overcome a significant energy barrier (low $-\Delta G_{hyd}°$ values), such as ClO_4^- and I^-, which are breakers of the water structure, enhance the rate of electron transfer relative to the other anions.

Figure 2 also shows the line from the data obtained earlier for the quenching of $^{*}Ru(bpy)_3^{2+}$ by MV^{2+}.[2] It is notable that the correlations have distinctly different slopes with the greatest difference between $^{*}Ru(bpy)_3^{2+}$ and $^{*}Ru(phen)_3^{2+}$ occurring for the anions with low $-\Delta G_{hyd}°$ values and accordance occurring at the higher values where $\lambda \approx 1.4-1.5$ eV. Interestingly, λ shows this same upper value as well for the quenching of both $^{*}Ru(bpy)_3^{2+}$ and $^{*}Ru(phen)_3^{2+}$ by MV^{2+} at low ionic strength (~1 mM) in the absence of any added electrolyte or buffer.[23] We believe that this upper value of λ represents the intrinsic reorganization energy of the solvent ($\lambda \approx \lambda_{out}$) intimately associated with these particular reactant cations;[24] anions, such as $H_2PO_4^-$, which have high values of $-\Delta G_{hyd}°$, are structure-makers and apparently do not affect the reorganization of the water upon electron transfer.

The same treatment of the data for $Ru(Clphen)_3^{2+}$ and $Ru(Me_2phen)_3^{2+}$ yields values of λ that are given in Table 3; unfortunately, the low solubility of those complexes in 0.1 M $NaClO_4$ precluded the obtaining of data for that salt. Nevertheless, even with the ±10% estimated uncertainty in λ, it is clear that on the average the reorganization energies for the quenching of the excited states of the tris-phenanthroline complexes by MV^{2+} are a function of the nature of the supporting electrolyte ($NaClO_4 < NaI < NaBr < NaCl < NaF < NaH_2PO_4$) and the nature of the ring substituents (Clphen < phen < Me_2phen). The maximum value of λ shown for the systems is 1.5 eV.

The variations in $\Delta G_{et}°$ and λ can be attributed to the electron-withdrawing and -donating characteristics of the substituents on the phenanthroline ligands. The chloro substituent, being electron-withdrawing, renders the reduced ligand in the excited-state electron poorer compared to phen, thereby rendering its oxidation potential less positive and lowering the driving force for electron transfer; the opposite situation holds for the methyl groups, which are electron-donating. The lower charge density on the Clphen ligand (compared to phen) reduces the local electrostatic interactions between the complex and the H_2O molecules associated with the counterions in the electron-transfer cage, in effect resulting in "structure-breaking" and a lower value of λ; again, the opposite situation holds for Me_2phen, which becomes a "structure-maker" with a higher value of λ. We see that this effect essentially disappears in the presence of NaH_2PO_4 and, of course, in the absence of added electrolytes.

In summary, this work demonstrates that the anion effect on the quenching reaction of cations is general in aqueous solution, and that the problem is quite severe to find a truly homologous series with which to apply Marcus theory, in particular plots of log k_{et} vs $\Delta G_{et}°$, the use of which assumes a constancy in the values of λ for all the species involved.

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Supporting Information Available: Tables of k_d, k_{-d}, and k_{et} as functions of temperature (3 pages). Ordering information is given on any current masthead page.

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