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COMMENTS

Comment on “Marcus Inverted Region in the Photoinduced Electron Transfer Reactions of Ruthenium(II)−Polypyridine Complexes with Phenolate Ions”

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In a recent paper in this journal, Thanasekaran et al.[1] reported on the observation of the Marcus inverted region in the reductive quenching of the MLCT excited states of Ru(II)−diimine complexes by phenolate ions in aqueous solution. Although inverted Marcus behavior is well established in intramolecular electron transfer,[2] there are very few unequivocal examples in intermolecular systems.[3]

The assignment of inverted Marcus behavior by Thanasekaran et al.[1] rests entirely on their values of k_q for the quenching of *Ru(bpz)$_3^{2+}$ (bpz = 2,2′-bipyrazine) by the phenolate ions. In Figure 5 of the paper, which shows a plot of log k_q vs $-\Delta G°$ for quenching by PhO$^-$ (phenolate ion), five points (for *Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine), *Ru(bpm)$_3^{2+}$ (bpm = 2,2′-bipyrimidine), *Ru(dmbpy)$_3^{2+}$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine), *Ru(phen)$_3^{2+}$ (phen = 1,10-phenanthroline), and *Ru(dpp)$_3^{2+}$ (dpp = 2,3-bis[2-pyridyl]pyrazine)) exhibit an increase in k_q with increasing exoergicity (normal Marcus behavior); the point for *Ru(bpz)$_3^{2+}$ dramatically breaks this trend. Indeed, the data in Table 2 of the paper show the same trends for 4-methylphenolate ion (4-CH$_3$PhO$^-$), 4-methoxyphenolate ion (4-CH$_3$OPhO$^-$), and 2,6-dimethylphenolate ion. In all the cases, the data for *Ru(bpz)$_3^{2+}$ do not fall on the anticipated Rehm−Weller plot with k_q approaching the diffusion-controlled limit as $\Delta G°$ becomes more negative.[4]

In the course of our examination of ground- and excited-state interactions between Ru(II)−diimine complexes and phenols,[5] we determined k_q for the reductive quenching of *Ru(bpy)$_3^{2+}$, *Ru(phen)$_3^{2+}$, *Ru(bpz)$_3^{2+}$, *Ru(bpz)$_2$(bpm)$^{2+}$, *Ru(bpz)$_2$(bpy)$^{2+}$, *Ru(bpm)$_2$(bpz)$^{2+}$, and *Ru(bpz)(bpm)(bpy)$^{2+}$ by PhO$^-$ and for *Ru(bpz)$_3^{2+}$ by a large number of chlorophenolate and para-substituted phenolate ions at pH 12.0 as a function of temperature.[6] To evaluate the driving forces of the quenching reactions, we determined the standard oxidation potentials (E_{ox}°) for the phenolate ions in aqueous solution[7] by use of the electrochemical technique of Andrieux and Saveant.[8] Values of the excited-state reduction potentials (*E_{red}°) of the bpy, bpz, and bpm complexes in aqueous solution were taken from the literature;[9] the potential of Ru(phen)$_3^{2+}$ is virtually the same as that for Ru(bpy)$_3^{2+}$.[10]

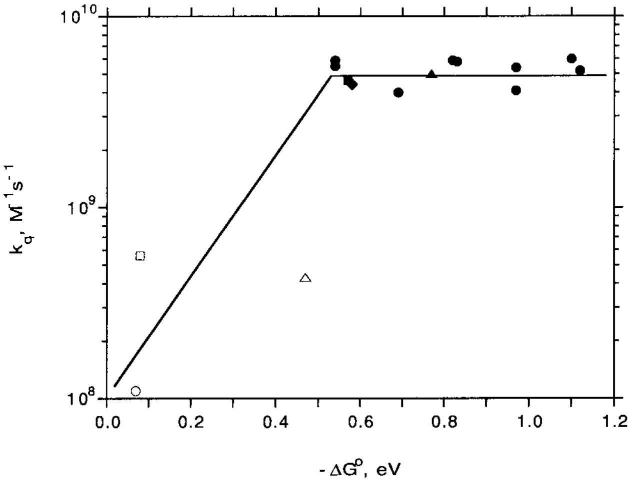

Figure 1. Plot of log k_q vs $-\Delta G°$ for the reductive quenching of *Ru(II) complexes by phenolate ions in Ar-purged aqueous solutions at pH 12.0 and 20 °C (μ = 0.05 with Na$_2$SO$_4$): *Ru(bpy)$_3^{2+}$ (○), *Ru(phen)$_3^{2+}$ (□), *Ru(bpz)$_3^{2+}$ (●), *Ru(bpz)$_2$(bpm)$^{2+}$ (▲), *Ru(bpz)$_2$(bpy)$^{2+}$ (◆), *Ru(bpm)$_2$(bpz)$^{2+}$ (■), *Ru(bpz)(bpm)(bpy)$^{2+}$ (△).

Table 1 shows our data; a direct comparison can be made with those of Thanasekaran et al.[1] for the same systems. We are surprised to find that our value of k_q for the *Ru(bpz)$_3^{2+}$−PhO$^-$ system is almost 40 times higher than that of Thanasekaran et al.[1] Further, although our value of k_q for *Ru(bpy)$_3^{2+}$−PhO$^-$ is virtually identical to that reported by Miedlar and Das,[11] it is a factor of 2 lower than that of Thanasekaran et al.[1] Moreover, our values for *Ru(bpz)$_3^{2+}$ with 4-CH$_3$PhO$^-$ and 4-CH$_3$OPhO$^-$ are about an order of magnitude higher. These

TABLE 1: k_q (10^9 M^{-1} s^{-1}) and $\Delta G°$ (eV) Values for the Reductive Quenching of *Ru(II) Complexes by Phenolate Ions in Aqueous Solution at pH 12.0 and 20 °C (μ = 0.05 M with Na$_2$SO$_4$)[a]

phenolate ion substituent[b]	Ru(yyy)$^{2+}$ (0.93 V)[c]		Ru(nnn)$^{2+}$ (0.94 V)[c]		Ru(zzz)$^{2+}$ (1.68 V)[c]		Ru(zzm)$^{2+}$ (1.63 V)[c]		Ru(zzy)$^{2+}$ (1.44 V)[c]		Ru(mmz)$^{2+}$ (1.43 V)[c]		Ru(zmy)$^{2+}$ (1.33 V)[c]	
	$-\Delta G°$	k_q	$-\Delta G°$	k_q	$-\Delta G°$	k_q	$-\Delta G°$	k_q	$-\Delta G°$	k_q	$-\Delta G°$	k_q	$-\Delta G°$	k_q
H (−0.86 V)	0.07	0.11	0.08	0.56	0.82	5.9	0.77	5.0	0.58	4.4	0.57	4.6	0.47	0.43
4-CH$_3$ (−0.71 V)					0.97	4.1								
4-CH$_3$O (−0.58 V)					1.10	6.0								
4-C$_2$H$_5$O (−0.56 V)					1.12	5.2								
4-CN (−1.14 V)					0.54	5.9								
4-CHO (−1.14 V)					0.54	5.5								
4-Cl (−0.85 V)					0.83	5.8								
pentachloro (−0.99 V)					0.69	4.0								
4-C$_2$H$_5$ (−0.71 V)					0.97	5.4								

[a] Abbreviations for the ligands: b = bpy; n = phen; z = bpz; m = bpm. [b] Values in parentheses are the oxidation potentials (vs NHE) of the phenolate ions in aqueous solution. [c] Excited-state reduction potential (vs NHE) in aqueous solution.

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differences in the data cannot be reconciled by differences in the temperatures and ionic strengths of the measurements. Table 1 also shows our values of k_q for the other excited complexes with PhO^- and for $*Ru(bpz)_3^{2+}$ with phenolate ions that cover a wide range of $\Delta G°$; the values of k_q for the latter systems average $(5.3 \pm 0.7) \times 10^9$ M^{-1} s^{-1}. A plot of log k_q vs $-\Delta G°$ is given in Figure 1, which clearly shows Rehm−Weller behavior.

We do not know the origin of the disparity between our data and those of Thanasekaran et al.;[1] it is well established that values of k_q can be easily reproduced as long as great care is taken to control the temperature and the nature of the solution medium.[12] Nevertheless, we are forced to conclude from the evidence on hand that the report by Thanasekaran et al.[1] cannot be taken as an experimental observation of the Marcus inverted region in bimolecular quenching reactions at the present time.

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