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Does back electron transfer within geminate redox pairs formed in bimolecular quenching follow a Marcus bell-shaped energy gap dependence?

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Abstract

The temperature dependence of the cage escape yield (η_{ce}) of redox products from the quenching of $^*Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by aromatic amines in deaerated 1:1 (v/v) CH_3CN/H_2O solutions has been examined. Values of λ, the solvent reorganization energy upon electron transfer within the geminate redox pairs, have been extracted from plots of $\log((\eta_{ce}^{-1}-1)T^{1/2})$ vs. $1/T$; the more sterically hindered two-ring amines exhibit a higher value of λ (1.1 ± 0.08 eV) than do most of the one-ring amines (0.82 ± 0.04 eV). A Marcus plot of $\log(\eta_{ce}^{-1}-1)$ vs. ΔG_{bt}^0 shows a correlation within only the inverted region for systems with the same λ; the earlier identification of the results for the same photosensitizer and quenchers as a bell-shaped energy-gap curve is due to the coincidental overlap of two independent segments within the inverted region.

Keywords: Back electron transfer; Geminate redox pairs; Bimolecular quenching; Marcus bell-shaped energy dependence

The Marcus theory predicts that the rate constant of electron transfer will follow a bell-shaped energy gap dependence as a function of ΔG_{ct}^0, initially increasing as ΔG_{ct}^0 becomes more negative in the normal region and decreasing with increasing driving force in the inverted region [1]. For excited-state redox quenching, both weak and strong Marcus dependences of the electron transfer rate constants within geminate redox pairs on driving force have been recorded, generally within the inverted region; occasionally, full bell-shaped curves have been observed. Ohno et al. [2] found well-defined bell-shaped curves for the rate constants k_{bt} of back electron transfer within the geminate redox pairs that are formed in the bimolecular reductive quenching of a series of excited Ru(II)–diimine complexes by aromatic amines in mixed CH_3CN–H_2O solutions. On the contrary, weak or no energy gap dependences of k_{bt} for both reductive [3] and oxidative [4,5] quenching have also been seen.

These seemingly disparate observations raise the question of the generality of the bell-shaped energy gap dependence for k_{bt} in the geminate redox pair generated in excited-state quenching. In order to explore this question, we have measured the temperature dependence of the efficiency η_{ce} of cage escape of the redox products released into solution for the quenching of $^*Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by the same aromatic amines (A) that were used previously [2]; in addition, two other amines were included to extend the series. The quenching reaction generates the reduced photosensitizer and the oxidized amine as a geminate pair, $[Ru(bpy)_3^{+}...A^{\bullet+}]$, within the solvent cage. The value of η_{ce} can be viewed, according to the conventional cage escape model [6], as arising from competitive back electron transfer (k_{bt}) and diffusional cage escape (k_{ce}). Thus $\eta_{ce} = k_{ce}/(k_{ce}+k_{bt})$ and $\eta_{ce}^{-1} - 1 = k_{bt}/k_{ce}$. In the previous studies, the assumption was made that k_{ce} is constant for the series of quenchers used, allowing an analysis to be made of the dependence of k_{bt} on the driving force ΔG_{bt}^0 of the reaction.

Nine amines were used as reductive quenchers in Ar-purged 1:1 (v/v) CH_3CN:H_2O solutions at ambient ionic strength with 25 μM $Ru(bpy)_3^{2+}$ and 0.02–15 mM A. Transient absorption and emission measurements were made with a Nd-doped yttrium aluminum garnet laser system (λ_{ex} = 532 nm) [7]; solution temperature within the optical cell were controlled at 10–60 (±0.1) °C. The quantum yield

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Table 1
Values of $\eta_{\rm ce}$ as a function of temperature, $E^0(\mathrm{A}^{\cdot +}/\mathrm{A})$ and λ for the amines used in the reductive quenching of $^*\mathrm{Ru(bpy)_3}^{2+}$

Amine	$E^0(\mathrm{A}^{\cdot +}/\mathrm{A})$ [a] (V)	$\eta_{\rm ce}$ [b]						λ (eV)
		10 °C	20 °C	30 °C	40 °C	50 °C	60 °C	
1 TMPD	0.21	0.53	0.57	0.68	0.66	0.67	0.71	0.85
2 PD	0.34	0.44	0.49	0.50	0.49	0.51	0.50	0.78
3 TMB	0.48	0.23	0.33	0.32	0.39	0.41	0.40	1.1
4 DMB	0.63	0.25	0.36	0.35	0.37	0.41	0.45	1.2
5 pheno	0.64	0.41	0.53	0.46	0.45	0.51	0.51	1.0
6 *p*-anis	0.68	0.72	0.68	0.62	0.61	0.58	0.60	0.84
7 *p*-tol	0.87 [c]	0.57	0.54	0.65	0.51	0.74	0.75	1.0
8 DPA	0.93 [c]	0.40	0.65	0.53	0.58	0.49	0.59	1.1
9 DMA	0.92 [c]	0.50	0.74	0.79	0.65	0.81	0.75	1.0

TMPD, *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine; PD, 1,4-phenylenediamine; TMB, 3,3′,5,5′-tetramethylbenzidine; DMB, 3,3′-dimethylbenzidine; pheno, phenothiazine; *p*-anis, *p*-anisidine; *p*-tol, *p*-toluidine; DPA, diphenylamine; DMA, *N,N*-dimethylaniline.

[a] E^0 vs. NHE. From cyclic voltammetry measurements on Ar-purged 1:1 (v/v) $\mathrm{CH_3CN:H_2O}$ solutions containing 0.1 M tetraethylammonium perchlorate and 2 mM amine at 0.1 V $\mathrm{s^{-1}}$ scan rate with a glassy carbon working electrode, Ag/AgCl reference electrode, Pt counterelectrode, and ferrocene as an internal standard.

[b] Average standard deviation of all the values of $\eta_{\rm ce} = \pm 8\%$ with a range of ± 4–12%.

[c] Fast-scan cyclic voltammetry (1000 V $\mathrm{s^{-1}}$) with the same electrochemical cell set-up

of cage escape was determined[1] from $\Phi = \Delta[\mathrm{A}^{\cdot +}]/\Delta[^*\mathrm{Ru(bpy)_3}^{2+}]$. Values of $\eta_{\rm ce}$ as a function of temperature (Table 1) were calculated from $(\Phi k_{\rm obs})/(k_{\rm obs} - k_0)$, where k_0 and $k_{\rm obs}$ are the first-order rate constants for the decay of the emission from $^*\mathrm{Ru(bpy)_3}^{2+}$ at 605 nm in the absence and presence respectively of quencher. Values of $\Delta G_{\rm bt}^0$ were calculated from a knowledge of $E^0(\mathrm{Ru}^{2+}/^+)$ (-1.13 V vs. a normal hydrogen electrode (NHE) in the same solvent system), $E^0(\mathrm{A}^{\cdot +}/\mathrm{A})$ (Table 1) and the coulombic work (approximately 10^{-2} eV) [9].

Plots of $\log(\eta_{\rm ce}^{-1} - 1)$ vs. $\Delta G_{\rm bt}^0$ at a fixed temperature resemble the bell-shaped curves reported by Ohno et al. [2a], with a maximum at -1.7 eV at 20 °C. According to the Marcus theory, the maximum of the bell-shaped curve occurs when the reorganization energy λ, which is a measure of the free energy required to move all the atoms, including the solvent shell, from their equilibrium positions in the precursor complex to that in the successor complex equals $-\Delta G_{\rm et}^0$. However, a value of -1.7 eV for λ is quite high in comparison with recently obtained values: about 1 eV for intramolecular electron transfer reactions in $\mathrm{CH_3CN}$ [4,10] and about 0.8 eV for the intermolecular reductive quenching of $^*\mathrm{Ru(bpy)_3}^{2+}$ by aromatic amines in protic solvents [11].

In general, the values of $\eta_{\rm ce}$ increase with increasing temperature (Table 1); variations for an individual quencher reflect the different complex temperature dependences of $k_{\rm bt}$ and $k_{\rm ce}$. The temperature dependence of $k_{\rm ce}$[2] is due to the variation in solution viscosity and dielectric constant, as well as to terms explicitly in T. If one assumes that $k_{\rm ce}$ is the same for all the amines, as has been done previously, its temperature dependence can easily be evaluated, permitting $k_{\rm bt}$ to be calculated as a function of temperature. Now, electron transfer within solvent-separated geminate radical ion pairs that are formed in quenching reactions is, in general, considered to be non-adiabatic (poor coupling) [2]. In the classical formulation of the Marcus theory, the rate constant of non-adiabatic electron transfer is given by the equation

$$k_{\rm et} = \frac{4\pi^2 V^2}{h(4\pi\lambda kT)^{1/2}} \exp\left(\frac{-(\lambda + \Delta G_{\rm et}^0)^2}{4\lambda kT}\right) \qquad (1)$$

where V is the electronic coupling coefficient and k is Boltzmann's constant. In general, λ can be determined from the slopes of linear plots of $\ln(k_{\rm et}T^{1/2})$ vs. $1/T$ [4a,10,13]. We obtained values of λ, which are the same whether plots of $\log(k_{\rm bt}T^*)$ or $\log[(\eta_{\rm ce}^{-1} - 1)T^{1/2}]$ vs. $1/T$ are used. The results are given in Table 1.

The significant result here is that the more sterically hindered two-ring systems exh[illegible] igher value of λ (1.1 ± 0.08 eV) than do the majority of the [illegible] ng systems (0.82 ± 0.04 eV); similar steric effects o[illegible] ave recently been reported [14]. The one-ring amines, [illegible] ol and DMA, are atypical with λ values of 1.0 eV, which most probably arise from variations in λ with the nature of the amine (tertiary vs. primary), as observed by Tazuke and coworkers [15] for the quenching reaction. Thus the nature, size and steric restrictions of the

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[1] Values of $\Delta[^*\mathrm{Ru(bpy)_3}^{2+}]$ were calculated from ΔA at 450 nm, extrapolated to the midpoint of the 7 ns laser pulse, in the absence of quencher, using $\Delta A = \Delta\epsilon l\,\Delta c$, where $\Delta\epsilon$ is the difference in the ϵ values at 450 nm of the excited- and ground-state photosensitizer (-1.0×10^4 $\mathrm{M^{-1}\,cm^{-1}}$) [8], $l = 2$ cm and Δc is the change in the concentrations of the absorbing species. Values of $\Delta[\mathrm{A}^{\cdot +}]$ were obtained 1–5 μs after the pulse, using $\Delta\epsilon$ values from the literature [2a].

[2] Values of $k_{\rm ce}$ (1.4×10^9 and 4.0×10^9 $\mathrm{s^{-1}}$ for TMB and PD respectively at 20 °C, for example) can be calculated as a function of temperature from the Melendar–Eigen [12] equation, which leads to an activation energy (19 kJ $\mathrm{mol^{-1}}$) that is independent of the quencher.

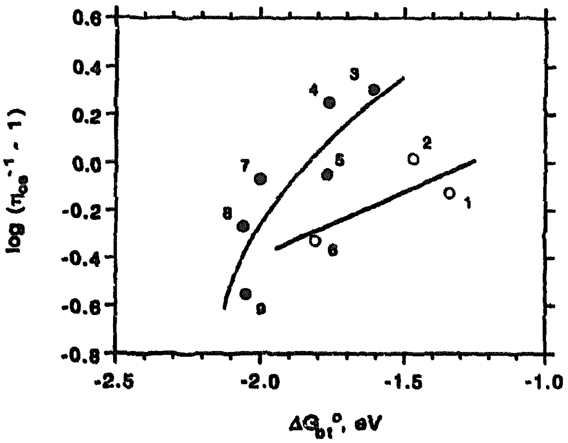

Fig. 1. Plot of $\log(\eta_{ce}^{-1}-1)$ vs. ΔG_{bt}^{0} at 20 °C for quenchers (see Table 1) with $\lambda = 1.1$ (± 0.08) eV (○) and $\lambda = 0.82$ (± 0.04) eV (●). The lines are drawn for ease of visualization and do not represent a theoretical fit.

quenchers contribute to the observed values of λ. The plot of $\log(\eta_{ce}^{-1}-1)$ vs. ΔG_{bt}^{0} in Fig. 1 groups together the quenchers with the same values of λ. The result is a correlation within only the inverted region, as observed recently with other systems [4,14].

We are forced to conclude that the earlier identification of the results for this system [2a] as a bell-shaped curve is due to the coincidental overlap of two independent segments within the inverted region; the earlier analysis of the data was based on the premise that λ for all the quenchers is the same, a situation that is clearly not the case. It is imperative in studies of this type that reaction rates be measured as a function of temperature in order to confirm the suspected Marcus behavior. Investigations of the dependence of rate constants of electron transfer on the driving force must include the careful choice of a truly homologous series of reactants, since differences in the structure and nature of the reactants can result in different values of λ, resulting in data that lie on different Marcus curves.

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