Pressure Effect on Photo-induced Electron-transfer Reactions between Tris-(2,2'-bipyridine)ruthenium(II) and Various Metal Complex Ions

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The electron-transfer quenching of photo-excited $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) by $[Mo(CN)_8]^{4-}$ and Eu_{aq}^{2+} gives large positive and negative activation volumes ($\Delta V^{\ddagger}$ +24.7 and −11.0 cm^3 mol^{-1}), respectively, whereas quenching by other quenchers having quenching rate constants of >10^9 mol^{-1} dm^3 s^{-1} has a negligibly small pressure effect regardless of the charge of quencher.

Studies of the pressure effect on the electron-transfer quenching of a photo-excited metal complex should provide a means for investigating the chemical behaviour of the excited state. Recently, Kirk and Porter reported a small pressure effect ($\Delta V^{\ddagger} = +0.5$ to -2.6 cm^3 mol^{-1}) on the quenching of photo-excited $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) by O_2, methyl viologen, and $[Co(acac)_3]$ (Hacac = acetylacetonate).[1] We have measured the effect of pressure (up to 300 MPa) on the electron-transfer quenching of photo-excited $[Ru(bpy)_3]^{2+}$ by various metal complex ions, and have found large pressure effects in some systems.†

Table 1 lists the quencher, the direction of electron transfer, the bimolecular quenching rate constant (k_q), and the activation volume ($\Delta V^{\ddagger}$). Typical Stern–Volmer plots are shown in Figure 1. The value of $\Delta V^{\ddagger}$ was calculated from equation (1), where k_0 and k_p are the quenching rate constants

$$-RT\ln(k_p/k_0) = \Delta V^{\ddagger}P + \Delta \beta^{\ddagger}P^2/2 \tag{1}$$

at atmospheric pressure and the applied pressure (P), respectively, and $\Delta \beta^{\ddagger}$ is the compressibility of activation. The quenching is of a dynamic nature, since k_q values obtained from the lifetime and the quantum yield measurements agreed well with each other for the quenching by $[Mo(CN)_8]^{4-}$.

The k_q values for the quenchers (1)—(6) are larger than 10^9 mol^{-1} dm^3 s^{-1} (probably diffusion-controlled), and the

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† Aqueous solutions of samples were deoxygenated and placed in a cylindrical quartz cell under N$_2$. The cell was placed in a high-pressure stainless-steel vessel with three sapphire windows, thermostatted at 25 °C. The concentration of $[Ru(bpy)_3]^{2+}$ was ca. 5 × 10^{-5} M (M = mol dm^{-3}) and concentrations of quenchers ranged from 10^{-3} to 10^{-1} M. Light from a dye laser of wavelength 450 nm with a ca. 3 ns pulse width (Molectron UV-24/DL-14) was used for excitation, and the luminescence decay was monitored at 620 nm. In the absence of quencher, the lifetime and the intensity of luminescence were not affected by pressure up to 300 MPa within an experimental error of ±10%. Decay of the excited state is much faster than succeeding reactions such as back electron transfer and decomposition of the primary reaction products (V. J. Holzwarth and H. Jurgensen, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 526; R. C. Young, F. R. Keene, and T. J. Meyer, *J. Am. Chem. Soc.*, 1977, **99**, 2468). Therefore the observed pressure effect can be ascribed to the pressure dependence of the electron-transfer process.
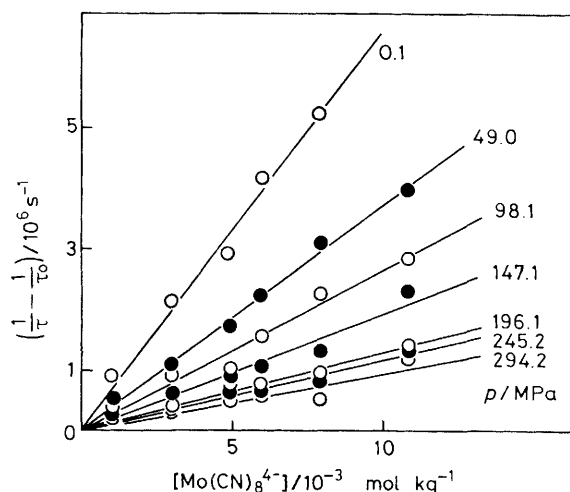

Figure 1. Stern–Volmer plot, $(1/\tau - 1/\tau_0)$ vs. $k_q[Q]$, for the lifetime quenching of photo-excited $[Ru(bpy)_3]^{2+}$ by $[Mo(CN)_8]^{4-}$ in 0.1 M HCl ($I = 0.25$ M, NaCl) at 25 °C.

Table 1. Activation volumes and rate constants for the quenching of photo-excited $[Ru(bpy)_3]^{2+}$.

	Quencher	Product[a]	$\Delta V^{\ddagger}/cm^3\ mol^{-1}$	$k_q/10^9\ mol^{-1}\ dm^3\ s^{-1\ b,h}$
(1)	$[Fe(CN)_6]^{3-}$ [c]	$[Ru]^{3+} + Q^-$	0.0 ± 0.1	5.6
(2)	$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(en)_2]^{4+}$ [d]	$[Ru]^{3+} + Q^-$	0 to $+1.0$	1.9
(3)	$[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+}$ [d]	$[Ru]^{3+} + Q^-$	$+1 \pm 2$	1.9
(4)	$[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]^{6-}$ [c]	$[Ru]^{3+} + Q^-$	0 to $+1.2$	4.8
(5)	Tl^{3+} [e]	$[Ru]^{3+} + Q^-$	$+0.2 \pm 0.1$	1.02
(6)	$[Fe(CN)_6]^{4-}$ [f]	$[Ru]^+ + Q^+$	0.0 ± 0.5	3.0
(7)	$[Mo(CN)_8]^{4-}$ [c]	$[Ru]^+ + Q^+$	$+24.7 \pm 0.6$	0.63
(8)	$[Os(CN)_6]^{4-}$ [c]	$[Ru]^+ + Q^+$	$+6.8 \pm 2.0$	0.84
(9)	$[IrCl_6]^{3-}$ [c]	$[Ru]^+ + Q^+$	$+1.1 \pm 0.5$	0.83
(10)	Eu_{aq}^{2+} [g]	$[Ru]^+ + Q^+$	-11.0 ± 1.0	0.0082
(11)	$[Fe(H_2O)_6]^{2+}$ [d]	$[Ru]^+ + Q^+$	-0.6 ± 0.6	0.01
(12)	$[Co(NH_3)_5(H_2O)]^{3+}$ [d]	$[Ru]^{2+} + {}^*Q$	-2.6 ± 0.6	0.14

[a] $[Ru]^{3+} + Q^-$, quencher is reduced by $^*[Ru]^{2+}$; $[Ru]^+ + Q^+$, quencher is oxidised by $^*[Ru]^{2+}$; $[Ru]^{2+} + {}^*Q$, quencher is sensitized by $^*[Ru]^{2+}$ (see V. Balzani, L. Moggi, M. F. Manfrin, and F. Bolletta, *Coord. Chem. Rev.*, 1975, **15**, 347). [b] k_q, bimolecular quenching rate constant at 25 °C, 1 atm. [c] 0.1 M HCl, $I = 0.25$ M (NaCl). [d] 0.05 M H_2SO_4, $I = 0.25$ M (NaCl); en = ethylenediamine. [e] 4.75 M $HClO_4$. [f] pH 5.2 (acetate buffer, 0.02 M), $I = 0.5$ M (NaCl). [g] 0.5 M $HClO_4$. [h] k_q values at atmospheric pressure have been reported, but the conditions for the measurements are different in some cases from ours: systems (1) and (6)—(8), A. Juris, M. T. Gandolfi, M. F. Manfrin, and V. Balzani, *J. Am. Chem. Soc.*, 1976, **98**, 1047; systems (2) and (3), K. Chandrasekaran and P. Natarajan, *Inorg. Chem.*, 1980, **19**, 1714; system (5), G. S. Laurence and V. Balzani, *Inorg. Chem.*, 1974, **13**, 2976; system (9), F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Phys. Chem.*, 1974, **78**, 1374; systems (10) and (11), ref. 2(a); system (12), G. Navon and N. Sutin, *Inorg. Chem.*, 1974, **13**, 2159.

$\Delta V^{\ddagger}$ values are in the range 0 to $+1\ cm^3\ mol^{-1}$. Quenching reactions in water, the rate of which is controlled by diffusion, are claimed to lead to a small pressure dependence.[1] The k_q values for the other quenchers (7)—(11), which act as reducing agents, are appreciably smaller than those for the quenchers (1)—(6). They give a varying pressure effect, the $\Delta V^{\ddagger}$ values ranging from $+24.7$ to $-11.0\ cm^3\ mol^{-1}$. The $\Delta V^{\ddagger}$ values do not seem to be related to k_q values and the charge of quencher. Quenchers with the same charge [(7), (8); (10), (11)] give significantly different $\Delta V^{\ddagger}$ values. The relationship between the observed k_q values and $\Delta G^{\ddagger}$ has been interpreted successfully by the Marcus theory for some of the systems in Table 1.[2] Stranks' method[3] of evaluation of $\Delta V^{\ddagger}$ on the basis of the Marcus theory, however, does not give a satisfactory interpretation for most of the observed $\Delta V^{\ddagger}$ values.‡

References

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2 (a) C. Creutz and N. Sutin, *Inorg. Chem.*, 1976, **15**, 496; (b) H. Toma and C. Creutz, *ibid.*, 1977, **16**, 545; (c) C. Creutz, *ibid.*, 1978, **17**, 1046.
3 D. R. Stranks, *Pure Appl. Chem.*, 1974, **38**, 303.

‡ The values of $\Delta V^{\ddagger}$ calculated in this way were $-12.1\ cm^3\ mol^{-1}$ for Eu_{aq}^{2+} and $[Fe(H_2O)_6]^{2+}$, $+5.5\ cm^3\ mol^{-1}$ for $[IrCl_6]^{3-}$, and $+10.1\ cm^3\ mol^{-1}$ for $[Mo(CN)_8]^{4-}$ and $[Os(CN)_6]^{4-}$.