The Quenching of Excited Uranyl Ion by d^6 Metallocenes

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Quenching constants k_Q of uranyl luminescence by d^6 metallocenes of Fe, Ru, and Os have been obtained both from luminescence intensity and lifetime measurements. The values of $\log_{10} k_Q$ are correlated with the oxidation potentials of metallocenes, in accordance with an electron-transfer mechanism. This scheme is supported by photoreaction studies, where the formation of either the rather elusive $[UO_2]^+$ ion or (in the case of osmocene solutions) uranium(IV) species has been observed: in the case of ferrocene solutions, ferricenium ion is also produced.

THE quenching of $[UO_2]^{2+}$ emission in solution has been extensively investigated in connection with photochemical studies[1] and a wide range of organic molecules and inorganic ions have been used as quenchers. A diversity of mechanisms seems to be involved,[2-6] but all of these are essentially chemical in nature, since the logarithms of the Stern–Volmer constants (K_{SV}) can be correlated either with the corresponding photochemical quantum yields of formation of U^{IV} or with the ionisation potential of the quencher. The latter correlation has been reported for the quenching of $[UO_2]^{2+}$ luminescence by aromatic hydrocarbons (prompting the suggestion of an exciplex mechanism[3]) and also inorganic ions (possibly *via* complete electron transfer). Again, Burrows *et al.*[6] find that the quenching of $(UO_2^{2+})^*$ by some metal ions is a dynamic process in which intermolecular electron transfer is the predominant mechanism.

In the present work, quenching of uranyl emission by various d^6 metallocenes in acetone solution has been studied as an example of excited-state interaction between $[UO_2]^{2+}$ and metallocenes.

EXPERIMENTAL

Materials.—The compounds $[M(\eta\text{-}C_5H_5)_2]$ ($M = Fe$ or Ru) and ferrocene derivatives were obtained commercially. Sublimation or recrystallisations were carried out until the compounds were pure (according to optical spectra and m.p.). Benzoylruthenocene, 1,1′-dibenzoylruthenocene, (α-hydroxybenzyl)ruthenocene, and osmocene were prepared by previously reported routes.[7] Uranyl nitrate was of AnalaR quality and acetone was Merck Spectro material that was further purified before use by vacuum distillation from P_4O_{10}.

Apparatus.—Luminescence spectra were recorded on a Perkin-Elmer MPF-2A spectrofluorimeter at excitation and emission wavelength settings of 410 and 510 nm respectively. Measurements of the luminescence lifetime were made with a frequency-doubled model K-347 ruby laser (λ 347 nm) (J. K. Lasers Ltd.). Pulses were of *ca.* 50-ns duration and the emission of $(UO_2^{2+})^*$ was monitored at 510 nm and recorded with a Polaroid camera. Microsecond flash-photolysis experiments were performed on an Applied Photophysics model KR-10 flash-kinetic spectrophotometer.

Our customary procedure[8] was used to obtain irradiations

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[1] H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139.

[2] R. Matsushima, *J. Amer. Chem. Soc.*, 1972, **94**, 6010.

[3] R. Matsushima and S. Sakuraba, *J. Amer. Chem. Soc.*, 1971, **93**, 7143.

[4] R. Matsushima, H. Fujimora, and S. Sakuraba, *J.C.S. Faraday II*, 1974, 1702.

[5] Y. Yokoyama, M. Moriyasu, and S. Ikeda, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1329.

[6] H. D. Burrows, S. J. Formosinho, M. da Graca Miguel, and F. Pinto Coelho, *J.C.S. Faraday I*, 1976, 163.

[7] M. Rosenblum, ' Chemistry of the Iron Group Metallocenes,' Interscience, New York, 1965.

[8] O. Traverso and F. Scandola, *Inorg. Chim. Acta*, 1970, **4**, 493.

at 404 and 433 nm. Irradiations were performed using a 5-cm pathlength quartz cell filled (20 cm^3) with solution and housed in suitable cell holders. The incident light intensity was measured by means of the potassium tris(oxalato)-ferrate(III) actinometer and was of the order of 2×10^{-7} einstein s^{-1} (1 einstein = $N_A h\nu$ J mol^{-1}).

Procedures.—Quenching studies. Solutions of $[UO_2]^{2+}$ at a constant concentration (5×10^{-3} mol dm^{-3}) and the quencher were placed in a quartz cell and degassed by freeze–pump–thaw cycles. The luminescence spectrum of each sample was recorded and the relative emission yields determined as a function of quencher concentration. (The luminescence spectrum of $[UO_2]^{2+}$ was unaffected by the presence of any of the quenchers examined.) All the quenching data were expressed in the form of the Stern–Volmer plot, the gradient of which yields K_{SV}. The absolute quenching constant, k_Q, can be determined from K_{SV}, which equals $k_Q\tau_0$, after determination of the lifetime of $(UO_2^{2+})^*$ in acetone in the absence of the quencher, τ_0. This was effected by laser flash photolysis [as was the lifetime of $(UO_2^{2+})^*$ in the presence of quencher, Q]. Lifetime data are expressed in the form of the Stern–Volmer plot, $\tau_0/\tau = 1 + K_{SV}[Q]$.

RESULTS

Metallocenes of Fe, Ru, and Os having the d^6 configuration have been used as quenchers of $(UO_2^{2+})^*$. For all the metallocenes studied, the quenching strictly follows Stern–Volmer kinetics, *e.g.* Figure 1. Quenching constants obtained by monitoring emission intensity are identical with those obtained by determination of the emission lifetimes of $(UO_2^{2+})^*$ at various quencher concentrations, *e.g.* Figure 1. τ_0 for $(UO_2^{2+})^*$ in acetone, determined directly by laser flash photolysis, is 1.2×10^{-6}s. Data are collected in Table 1.

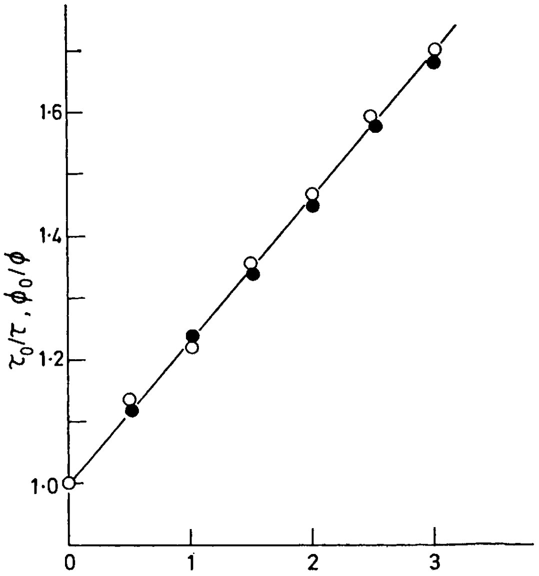

FIGURE 1 Quenching of uranyl luminescence by ruthenocene at 298 K: (○) luminescence intensity; (●) lifetime of $(UO_2^{2+})^*$, τ

Irradiation of degassed solutions of uranyl nitrate (5×10^{-2} mol dm^{-3}) in anhydrous acetone with light of wavelength either 404 or 433 nm caused no appreciable reaction. Irradiations were also performed using solutions containing uranyl nitrate (5×10^{-2} mol dm^{-3}) and ferrocene (2×10^{-3} mol dm^{-3}, at which concentration light absorption by ferrocene is negligible) when an increase in absorbance ($\lambda_{max.}$ 617 nm) was observed, indicating induced oxidation of ferrocene to ferricenium cation.[8] Additionally, new absorption peaks were gradually formed at 1 510, 960, and 830 nm (Figure 2), which coincide with those reported for $[UO_2]^+$ ion in dimethyl sulphoxide and other media.[9,10] The near-i.r. absorptions are, however, rather unstable and after *ca.* 30 min of photolysis their intensity decreases (with a general increase in the background) possibly because of oxidation of $[UO_2]^+$ by decomposition [8] products of the ferricenium cation. At the initial stages of photolysis the formation of ferricenium ion obeyed zero-order kinetics, enabling calculation of an apparent quantum yield (based on light absorbed by $[UO_2]^+$ ion).

TABLE 1

k_Q for the quenching of $[UO_2]^{2+}$ emission by d^6 metallocenes in acetone solution

Quencher	Lowest $\tilde{\nu}_{max.}$/ 10^{-3} cm^{-1}	k_Q/dm^3 mol^{-1} s^{-1}
(1) [Fe(η-C_5H_5)$_2$]	22.70	$(1.6 \pm 0.1) \times 10^{10}$
(2) [Fe(η-C_5H_5)(η-C_5H_4COPh)]	21.74	$(4.5 \pm 0.2) \times 10^9$
(3) [Fe(η-C_5H_5)(η-C_5H_4COMe)]	22.37	$(4.0 \pm 0.2) \times 10^9$
(4) [Ru(η-C_5H_5)$_2$]	31.25	$(2.1 \pm 0.1) \times 10^9$
(5) [Ru(η-C_5H_5){η-C_5H_4CH(OH)-Ph}]	31.50	$(1.30 \pm 0.06) \times 10^9$
(6) [Fe(η-C_5H_4COMe)$_2$]	22.30	$(1.00 \pm 0.05) \times 10^9$
(7) [Ru(η-C_5H_5)(η-C_5H_4COPh)]	30.15	$(5.7 \pm 0.3) \times 10^8$
(8) [Ru(η-C_5H_4COPh)$_2$]	29.50	$(3.0 \pm 0.15) \times 10^8$
(9) [Os(η-C_5H_5)$_2$]	29.70	$(4.2 \pm 0.04) \times 10^7$

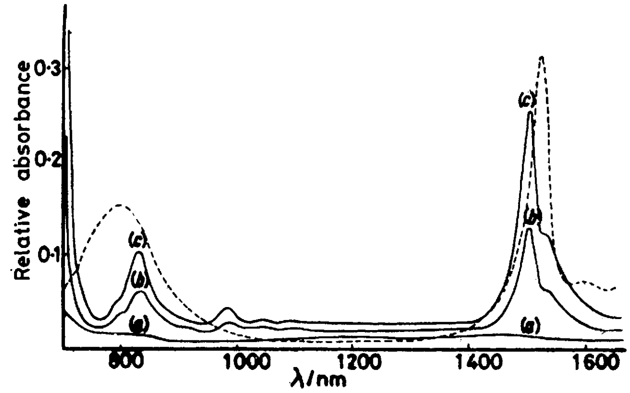

FIGURE 2 The electronic spectrum of uranyl nitrate (5×10^{-2} mol dm^{-3}) in the presence of ferrocene (2×10^{-3} mol dm^{-3}) undergoing photolysis (5-cm cell, λ 404 nm): (*a*) original uranyl solution; (*b*) after 10-min irradiation; (*c*) after 20-min irradiation; (– – –) $[UO_2]^+$ in molten LiCl–KCl at 720 K (ref. 10)

Photoreactions were also performed with deaerated solutions of uranyl nitrate (5×10^{-2} mol dm^{-3}) containing ruthenocene (2×10^{-3} mol dm^{-3}). While in these experiments we were unable to observe photo-oxidation of ruthenocene since the corresponding cation absorbs at 320 nm where both U^{VI} and U^V strongly absorb, photoproduction of $[UO_2]^+$ was again observed.

In contrast to the behaviour described above, photolysis of uranyl solutions in the presence of osmocene (2×10^{-3}

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[9] G. Gritzner and J. Selbin, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1799; L. Cohen, *ibid.*, 1970, **32**, 3525.

[10] D. A. Wenz, M. D. Adams, and R. K. Steunenberg, *Inorg. Chem.*, 1964, **3**, 989.

mol dm^{-3}) causes, in the first stage of photoreaction, formation of U^{IV} as indicated by an increase in absorption at 650 nm.[11] Flash photolysis of these degassed solutions also produces an absorption ($\lambda_{max.}$ 650 ± 10 nm) within 20 μs of the flash, indicating that U^{IV} is a primary photoproduct (rather than a secondary product formed by reduction or disproportionation of U^{V}). The presumed oxidised product of this two-electron transfer, $[Os(\eta\text{-}C_5H_5)_2]^{2+}$, was not detected optically and is known to be very unstable.[7]

DISCUSSION

The experimental results clearly show that d^6 metallocenes of Fe, Ru, and Os are strong quenchers of $(UO_2^{2+})^*$. As regards the mechanism, the most reasonable possibilities are: (A) electronic-energy transfer from $(UO_2^{2+})^*$ to the metallocenes; (B) external heavy-atom perturbation of $(UO_2^{2+})^*$ by assisted intersystem crossing; (C) electron transfer between $(UO_2^{2+})^*$ and metallocenes; and (D) exciplex quenching of $(UO_2^{2+})^*$ [*cf.* the quenching of $(UO_2^{2+})^*$ by aromatic hydrocarbons [3]]. Pertinent experimental results are: (*i*) the quenching is highly efficient (approaching the diffusion-controlled rate) with metallocene complexes which do not possess optically detectable electronic excited states below the emitting level of $(UO_2^{2+})^*$ (corrected emission maximum at 25 °C = 20 500 cm^{-1}); (*ii*) Ru- and Os-centred metallocenes do not quench as effectively as their Fe analogues; (*iii*) the production of either $[UO_2]^+$ or uranium(IV) species accompanies the photoreaction of $[UO_2]^{2+}$–$[M(\eta\text{-}C_5H_5)_2]$ systems. (*iv*) The oxidation of $[Fe(\eta\text{-}C_5H_5)_2]$ to $[Fe(\eta\text{-}C_5H_5)_2]^+$ by $(UO_2^{2+})^*$ has an apparent quantum yield $\Phi = 0.62$; and (*v*) log k_Q is linearly related to the standard oxidation potential ($E^\ominus$) of the quenching metal complexes (Figure 3).

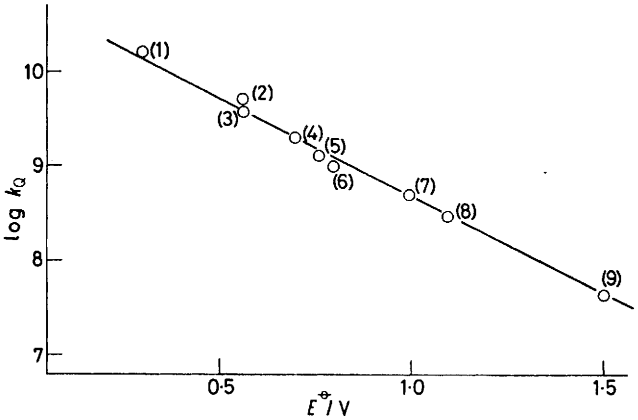

FIGURE 3 Correlation of log k_Q and $E^\ominus$ (metallocene) for quenching of $[UO_2]^{2+}$ luminescence. The numbers indicate the quenchers in Table 1

Mechanism (A) does not explain result (*v*); although reduction of $[UO_2]^{2+}$ by electronically excited $[M(\eta\text{-}C_5H_5)_2]$ could occur [to give results (*iii*) and (*iv*)], the correlation between k_Q and $E^\ominus$ is best explained by an electron transfer in the excited-state complex. Results (*ii*) and (*iii*) are inconsistent with mechanism (B); (*iii*) and (*iv*) rule out (D). However, all the above results are in accordance with mechanism (C). Thus, electron transfer from $(UO_2^{2+})^*$ to $[M(\eta\text{-}C_5H_5)_2]$ is energetically allowed since $(UO_2^{2+})^*$ with an electronic energy [12] of 20 500 cm^{-1} is expected to be a stronger oxidising agent than ground-state $[UO_2]^{2+}$ ($E^\ominus$ 0.062 V) by *ca.* 2.54 V, giving $E^\ominus(UO_2^{2+})^* = 2.60$ V. The oxidation potentials of the metallocene quenchers are listed in Table 2, and in each case the electron transfer to $(UO_2^{2+})^*$ is seen to be thermodynamically possible: indeed $\Delta G_Q^\ominus = E_Q^\ominus - E^\ominus(UO_2^{2+})^*$ is always more negative than -1.0 V. The observation of an excellent linear free-energy relation between the bimolecular quenching rate constant and the oxidation potential of the metallocene (Figure 3) parallels the behaviour reported in several studies of the quenching of $(UO_2^{2+})^*$, and strongly supports mechanism (C), which can be presented in detail in equations (1)—(5)

TABLE 2

Free-energy changes in the electron-transfer process between $(UO_2^{2+})^*$ and metallocenes

Metallocene	$E^\ominus$/V †	$-\Delta G_Q$/V
(1)	0.330	2.27
(2)	0.571	2.03
(3)	0.575	2.02
(4)	0.693	1.91
(5)	0.755	1.85
(6)	0.796	1.80
(7)	0.907	1.69
(8)	1.089	1.51
(9)	1.50	1.10

† From ref. 7; the data refer to one-electron changes except in the case of osmocene (which refers to a two-electron change).

$$[UO_2]^{2+} + h\nu \xrightarrow{I_a} (UO_2^{2+})^* \qquad (1)$$

$$(UO_2^{2+})^* \xrightarrow{k_F} [UO_2]^{2+} + h\nu_F \qquad (2)$$

$$(UO_2^{2+})^* \xrightarrow{k_D} [UO_2]^{2+} + \text{heat} \qquad (3)$$

$$(UO_2^{2+})^* + Q \xrightarrow{k_4} [UO_2]^+ + Q^+ \qquad (4)$$

$$(UO_2^{2+})^* + Q \xrightarrow{k_5} [UO_2]^{2+} + Q + \text{heat} \qquad (5)$$

where I_a = absorbed light intensity and Q refers to the metallocene quenchers. Under steady-state conditions for $(UO_2^{2+})^*$, equation (6) can be obtained where $\tau_0 = 1/(k_F + k_D)$, *i.e.* we can write (7).

$$I_{F^0}/I_F = 1 + \tau_0(k_4 + k_5)[Q] \qquad (6)$$

$$K_{SV} = \tau_0(k_4 + k_5) \qquad (7)$$

It is significant that, while quenching of $(UO_2^{2+})^*$ by $[Fe(\eta\text{-}C_5H_5)_2]$, $[Ru(\eta\text{-}C_5H_5)_2]$, and their derivatives apparently involves a one-electron transfer process, the quenching by $[Os(\eta\text{-}C_5H_5)_2]$ probably occurs by a two-electron transfer mechanism. While such a process explains the observed primary photoproduction of U^{IV}, there is no direct evidence for the immediate formation of the corresponding $[Os(\eta\text{-}C_5H_5)_2]^{2+}$ cation. Evidently the behaviour of the metallocenes of Fe and

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[11] L. J. Heidt, *J. Amer. Chem. Soc.*, 1954, **76**, 5962.

[12] J. T. Bell and R. E. Biggers, *J. Mol. Spectroscopy*, 1968, **25**, 312.

Ru in their quenching of $[UO_2]^{2+}$ luminescence reflects the trend observed in their chemical oxidation in which, while $[M(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) readily lose a single electron, $[Os(\eta\text{-}C_5H_5)_2]$ loses two electrons.[5]

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