Electron-transfer Chemistry of the Luminescent Excited State of *trans*-Dioxo-osmium(VI)†

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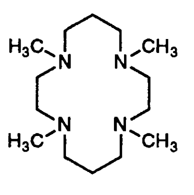
Excitation of *trans*-dioxo-osmium(VI) complexes in the solid state and in fluid solutions at room temperature at 350—400 nm results in red emission with maxima at 620—710 nm. Rate constants for electron-transfer quenching of *trans*-$[Os^{VI}(L^1)O_2]^{2+*}$ (L^1 = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) and *trans*-$[Os^{VI}(L^4)O_2]^{2+*}$ {L^4 =*meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene} by a series of structurally related aromatic hydrocarbons with varying redox potentials have been determined in acetonitrile. The ^3E_g states of *trans*-$[Os^{VI}(L^1)O_2]^{2+}$ and *trans*-$[Os^{VI}(L^4)O_2]^{2+}$ are powerful one-electron oxidants, the excited-state reduction potentials of which in acetonitrile, $E^\circ(Os^{VI*}-Os^{V})$, have been found to be 2.39(10) and 2.00(10) V *vs.* normal hydrogen electrode respectively, which agree well with estimations using spectroscopic and electrochemical data.

In recent years, there has been increased interest in the search for strongly luminescent inorganic reagents that act as powerful oxidants/reductants in the excited state.[1] It is this enhanced ability of excited states to function as better oxidants/reductants compared with the ground state that attracted researchers to look into the possibility of generating powerful photo-oxidants/reductants capable of producing highly unstable transient species. Moreover, it allows for the convenient study of the kinetics of highly exergonic electron-transfer reactions and provides additional opportunities for the evaluation of theories of electron transfer. Recent works in the generation of powerful inorganic photo-oxidants include the photochemistry of osmium(VI) nitrido and oxo complexes,[2a—d] metal 2,2′-bipyridine complexes,[2e—h] and gold(III) porphyrins.[2i] Although metalloporphyrins and metal-containing bipyridine complexes are commonly employed as photocatalysts, these species suffer from the disadvantage that long-lived excited states with potential greater than 2.0 V *vs* normal hydrogen electrode (n.h.e.) are difficult to generate because of the rapid intramolecular reductive quenching, which is an inevitable consequence of the π-unsaturated nature of the co-ordinated ligand.

Previous reports by Winkler and Gray[3] on the spectroscopic properties of *trans*-dioxorhenium(V) complexes aroused our interest in studying the isoelectronic *trans*-d^2-dioxo-osmium(VI) species,[2c,d] with the hope of developing powerful metal–oxo photo-oxidants through light excitation of the ground-state metal oxo complexes. Perhaps the most fundamental properties associated with electron-transfer reactivity are redox potentials. In an earlier communication[2c] we reported that *trans*-d^2-dioxo-osmium(VI) complexes are powerful photo-oxidants with an estimated excited-state redox potential of >2.0 V *vs.* n.h.e. for *trans*-$[Os^{VI}(L^1)O_2]^{2+*}$ (L^1 = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) using spectroscopic and electrochemical methods. Herein are reported the photophysical properties of a series of *trans*-d^2-dioxo-osmium(VI) complexes, and the completed studies of the reductive quenching of *trans*-$[Os^{VI}(L^1)O_2]^{2+*}$ and *trans*-$[Os^{VI}(L^4)O_2]^{2+*}$ {L^4 = *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene} by a series of aromatic hydrocarbons from which the excited-state redox potentials have been determined through the application of Marcus–Hush electron-transfer theory.[4]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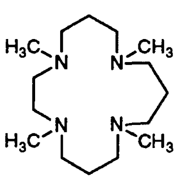
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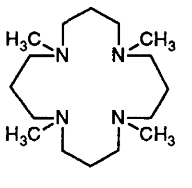
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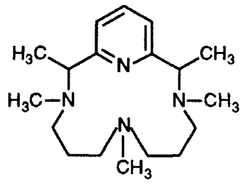
L^4

Experimental

The complexes *trans*-$[Os^{VI}(L)O_2][ClO_4]_2$ (L = L^1, L^2 = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane, L^3 = 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane, or L^4) were prepared as reported previously.[5a—c] An ethanolic solution of sodium hexachloro-osmate(IV) (0.5 g in 200 cm^3) was added dropwise to a refluxing ethanolic suspension of the ligand (0.5 g in 200 cm^3) and finely divided tin foil (2 g). The addition took 5 h to complete, and the reaction mixture was then refluxed for 12 h. It was filtered, and the filtrate rotary evaporated to dryness. The yellow residue was dissolved in deionized water (10 cm^3) and heated to *ca.* 80 °C for 15 min. The resulting yellow-green solution was filtered. To the filtrate was then slowly added hydrogen peroxide (50%, 1—2 cm^3). The solution was then cooled in an ice–water bath and upon addition of excess of sodium perchlorate, a yellow solid of *trans*-$[Os(L)O_2][ClO_4]_2$ slowly deposited. This was filtered off and yellow crystals of the

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

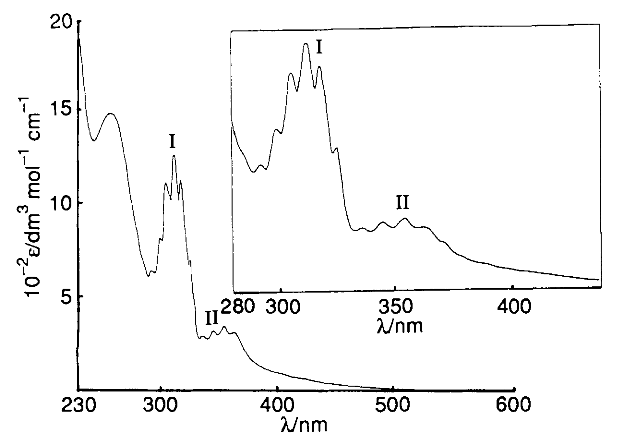

Figure 1. U.v.–visible spectrum of *trans*-$[Os(L^1)O_2][ClO_4]_2$ in acetonitrile

Table 1. U.v.–visible spectral data for *trans*-$[Os^{VI}(L)O_2]^{n}$ in MeCN at 25 °C

Complex	$\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}) $^1A_{1g} \longrightarrow {}^1E_g$	 $^1A_{1g} \longrightarrow {}^3E_g$
trans-$[Os(L^1)O_2]^{2+}$	312(1 260)	355(340)
trans-$[Os(L^2)O_2]^{2+}$	307(1 810)	347(480)
trans-$[Os(L^3)O_2]^{2+}$	306(1 910)	346(340)
trans-$[Os(L^4)O_2]^{2+}$	307(1 930)	365(370)
trans-$[Os(CN)_4O_2]^{2-}$	317(1 000)	370(300)

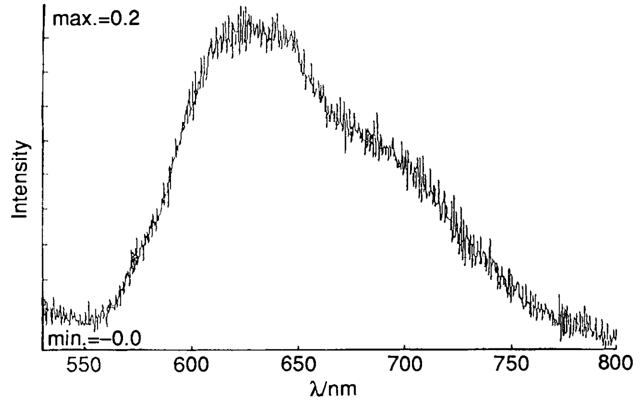

Figure 2. Emission spectrum of a polycrystalline sample of *trans*-$[Os(L^1)O_2][ClO_4]_2$ at 18 K with excitation at 355 nm

osmium complex were obtained by recrystallization from hot perchloric acid (0.1 mol dm^{-3}, 60 °C). The salt $[AsPh_4]_2$[*trans*-$Os^{VI}(CN)_4O_2$] was prepared according to the literature procedure.[5d] Acetonitrile (Mallinckrodt, ChromAR, HPLC grade) was distilled over calcium hydride and potassium permanganate before use. The aromatic hydrocarbons were purified according to literature procedures.[6]

U.v.–visible spectra were obtained on a Shimadzu UV-240 spectrophotometer. Steady-state emission spectra were recorded with or without Corning filters on a Hitachi 650-60 fluorescence spectrophotometer. Corrected emission spectra were obtained using a Hitachi 650-0178 data processor accessory. The absolute luminescence quantum yield was measured by the method of Demas and Crosby[7] using quinine sulphate as a standard.

Luminescence quenching experiments were monitored by time-resolved (lifetime) emission measurements, and data were treated by a Stern–Volmer fit as described by $\tau_0/\tau = 1 + k_q\tau_0[Q]$ where τ_0 and τ are the lifetimes in the absence and presence of quencher Q respectively. Emission lifetime measurements were performed using a time-resolved laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 Hz, G resonator). Luminescence decay signals were recorded either on a Tektronix model 2430 digital oscilloscope or a model 7912AD transient recorder with a 7B90P programmable time base, a 7A19 vertical amplifier, and a type 602 display unit. Acquisition of waveforms from selected Tektronix digitizers was performed on an Epson PCe IBM-XT compatible personal computer *via* a GPIB-PC2A interface card, using the Tekware GURU II software package for computer control. The waveforms were acquired and analysed using a program for exponential fit. All solutions for quenching studies were prepared under vacuum in a round-bottom flask (10 cm^3) with a sidearm fluorescence cuvette (1 cm) and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

The transient absorption spectra and kinetics were obtained using a conventional set-up with the output (355 nm) of a DCR-3 pulsed Nd-YAG laser as the excitation source. The monitoring beam was a tungsten iodide lamp source (100 W).

Results and Discussion

The electronic absorption spectrum of *trans*-$[Os(L^1)O_2][ClO_4]_2$ (Figure 1) in acetonitrile exhibits vibronically structured absorption bands in the regions 300—320 and 345—370 nm. The bands at 312 and 355 nm are assigned as the spin-allowed ($^1A_{1g} \longrightarrow {}^1E_g$) and spin-forbidden ($^1A_{1g} \longrightarrow {}^3E_g$) $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{\pi^*})^1$ transitions, respectively, which are vibronically coupled to the $A_{2u}(OsO_2)$ stretching mode ($d_{\pi^*} = d_{xz},d_{yz}$). With reference to previous work,[3] a ^3E_g state in D_{4h} symmetry and in the presence of a strong spin–orbit coupling perturbation will decompose into states of A_{1g}, A_{2g}, B_{1g}, B_{2g}, and E_g symmetries in the D_{4h}' double group, while the doubly degenerate ^1E_g state just correlates with a E_g level. The $E_g(^3E_g)$ level can acquire singlet character by mixing with the $E_g(^1E_g)$ state, and hence it should be the most intense of the transitions to states derived from ^3E_g. The band at 355 nm in Figure 1 is thus attributed to $^1A_{1g} \longrightarrow E_g(^3E_g)$ transition. Very weak absorptions at *ca.* 450—550 nm are also observed in the low-energy tail of the $^1A_{1g} \longrightarrow E_g(^3E_g)$ band, possibly attributed to the $^1A_{1g} \longrightarrow B_{1g}(^3E_g)$ and $^1A_{1g} \longrightarrow B_{2g}(^3E_g)$ transitions. U.v.–visible spectral data for other *trans*-d^2-dioxo-osmium(VI) complexes are collected in Table 1. The $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{\pi^*})^1$ transition of the *trans*-dioxo-osmium(VI) system is insensitive to the ring size of the macrocyclic ligands from L^1 to L^3 and to the nature of the equatorial ligand, in accord with the transition occurring within the d_π orbitals.[5a,8]

Excitation of *trans*-$[Os(L^1)O_2][ClO_4]_2$ at 350—400 nm results in red emission with a maximum at 620 nm. The spectrum at 18 K is shown in Figure 2. The photophysical data of other *trans*-d^2-dioxo-osmium(VI) complexes are included in Table 2. Since the most intense transition to states derived from ^3E_g is the $E_g(^3E_g)$ state, the large Stokes shift between the excitation and emission energies suggests that the emissive state is not $E_g(^3E_g)$, but rather it may be the low-lying spin–orbit B_{1g} or B_{2g} sublevel of the ^3E_g state. In accordance with this, the emission energies ($E_{0-0} \approx$ 2.0—2.2 eV) are relatively insensitive to the nature of the equatorial ligand. Unlike the *trans*-dioxo complexes of rhenium(V),[3b] there is only a small variation in the excited-state lifetime of *trans*-$[Os(L^1)O_2][ClO_4]_2$ in both protic and aprotic solvents, and neither the lifetime nor the intensity of the emission is quenched by protons. We postulate that this difference in reactivity toward protons can be attributed to the difference in acid–base properties of the *trans*-d^2-dioxo-

Table 2. Photophysical data for *trans*-$[Os^{VI}(L)O_2]^n$ in MeCN (0.1 mol dm^{-3} NEt_4ClO_4) at 25 °C

Complex	Emission $\lambda_{max.}$/nm	Lifetime/ μs	E_{0-0}/ eV	$E°$/V *vs.* n.h.e. Os^{VI}–Os^{V}	$E°$/V *vs.* n.h.e. Os^{VI*}–Os^{V}
trans-$[Os(L^1)O_2]^{2+}$	620	1.0^a			
		1.4^b			
		1.5^c	2.2	0.01^c	2.20^c
trans-$[Os(L^2)O_2]^{2+}$	625	1.0	2.2	−0.05	2.15
trans-$[Os(L^3)O_2]^{2+}$	600	1.6	2.2	−0.05	2.15
trans-$[Os(L^4)O_2]^{2+}$	710	0.9	2.0	−0.03	1.97
trans-$[Os(CN)_4O_2]^{2-}$	710	0.4	2.0	−0.88	1.12

^{a} Complex concentration = 0.275 mmol dm^{-3}. ^{b} In deionized water. ^{c} In 0.1 mol dm^{-3} CF_3CO_2H.

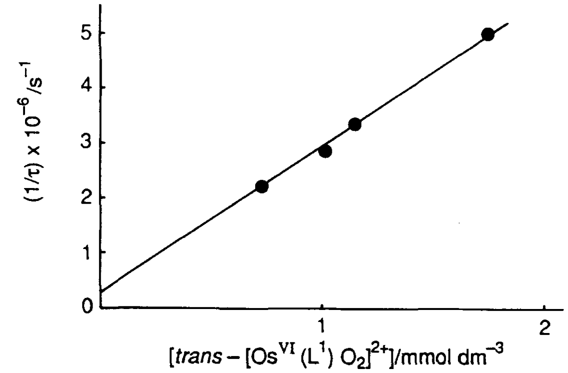

Figure 3. Plot of $1/\tau$ *versus* the concentration of *trans*-$[Os(L^1)O_2][ClO_4]_2$ in acetonitrile (0.1 mol dm^{-3} NEt_4ClO_4)

osmium(VI) and -rhenium(V) complexes. A higher pK_a value for the rhenium complex would be anticipated since the *trans*-dioxorhenium(V) complex with a smaller positive charge would show a higher affinity for protons than would the corresponding osmium(VI) complex [equations (1) and (2)].

$$[Re^{V}(L)O_2]^{+} + H^{+} \rightleftharpoons [Re^{V}(L)O(OH)]^{2+} \quad (1)$$

$$[Os^{VI}(L)O_2]^{2+} + H^{+} \rightleftharpoons [Os^{VI}(L)O(OH)]^{3+} \quad (2)$$

It is found that the phosphorescence of *trans*-$[Os^{VI}(L^1)O_2]^{2+*}$ displays a large excited-state lifetime dependence on the concentration of *trans*-$[Os^{VI}(L^1)O_2]^{2+}$ in acetonitrile, suggesting the existence of a self-quenching mechanism ($k_q = 2.6 \times 10^9$ dm^3 mol^{-1} s^{-1}) over a concentration range of 0.5—2.8 mmol dm^{-3} of *trans*-$[Os(L^1)O_2]^{2+}$ in 0.1 mol dm^{-3} NEt_4ClO_4 (MeCN). An inherent excited-state lifetime of 3.3 μs at room temperature has been obtained from a plot of $1/\tau$ *versus* concentration of *trans*-$[Os(L^1)O_2]^{2+}$ (Figure 3). Similarly, a self-quenching rate constant of 4.0×10^8 dm^3 mol^{-1} s^{-1} has been obtained for *trans*-$[Os^{VI}(L^4)O_2]^{2+*}$ in 0.1 mol dm^{-3} NEt_4ClO_4 (MeCN). On the contrary, *trans*-$[Os^{VI}(CN)_4O_2]^{2-*}$ shows no observable lifetime dependence over a concentration range of 0.7—3.6 mmol dm^{-3} in 0.1 mol dm^{-3} NEt_4ClO_4 (MeCN), possibly attributed to its short lifetime, which would render difficult the observation of self-quenching.

The luminescence quantum yield of *trans*-$[Os(L^1)O_2][ClO_4]_2$ in Barnstead 'nanopure' water was estimated to be $\leqslant 10^{-3}$ using quinine sulphate as the standard with excitation at 365 nm.

The excited-state redox potentials $E(Os^{VI*}$–$Os^{V})$ for the *trans*-$[Os^{VI}(L)O_2]^n$ complexes have been determined using spectroscopic and electrochemical estimations, $E°(Os^{VI*}$–$Os^{V}) = E°(Os^{VI}$–$Os^{V}) + E_{0-0}(Os^{VI}$–$Os^{VI*})$, where $E_{0-0}(Os^{VI}$–$Os^{VI*})$ is the zero–zero spectroscopic energy. Values of the standard reduction potential of the couple Os^{VI}–Os^{V} (0.01 V *vs.* n.h.e. in water)[9] from cyclic voltammetric studies and the estimated emission E_{0-0} (*ca.* 2.2 eV) for *trans*-$[Os(L^1)O_2]^{2+}$ obtained from the low-temperature emission spectrum of a solid crystalline sample of *trans*-$[Os(L^1)O_2][ClO_4]_2$ at 18 K (Figure 2) with 0—0 transition in the region 567—573 nm[8] suggest that its ^3E_g state $[(d_{xy})^1(d_{\pi*})^1]$ is an extremely powerful one-electron oxidant: $E°(Os^{VI*}$–$Os^{V}) \approx 2.2$ V *vs.* n.h.e. in water. The excited-state redox potentials for the other osmium(VI) complexes were similarly estimated and are summarized in Table 2.

Quenching by Alkylbenzenes.—Previous work showed that the phosphorescence of *trans*-$[Os(L^1)O_2]^{2+*}$ is quenched by organic substrates such as alkenes, alcohols, and amines.[2c,d] The systematic studies on electron-transfer reactions of aromatic hydrocarbons by Kochi and co-workers[10] and Reed and Murray[11] aroused our interest in employing this class of compounds as quenchers for the systematic study of electron-transfer quenching of the *trans*-dioxo-osmium(VI) system since a knowledge of the one-electron oxidation potential of the quenchers is readily accessible.

It is found that the phosphorescence of *trans*-$[Os(L^1)O_2]^{2+*}$ in acetonitrile is quenched by alkylbenzenes. Neither the electronic absorption nor the emission spectrum of *trans*-$[Os(L^1)O_2]^{2+}$ changes in the presence of the quenchers, and no evidence for the formation of new chemical species was observed in steady-state emission experiments. The measured rate constants corrected for the diffusion-controlled rates of luminescence quenching of *trans*-$[Os(L^1)O_2]^{2+*}$ by a series of alkylbenzenes are given in Table 3. The rate constants exhibit a dependence upon the ionization potential of the substituted benzenes. An excited-state reduction potential $E°(Os^{VI*}$–$Os^{V})$ of 2.39(10) V *vs.* n.h.e. has been obtained by three-parameter, non-linear-least-squares fits using equation (3)[12] where k_q' is

$$\left(\frac{RT}{F}\right)\ln k_q' = \left(\frac{RT}{F}\right)\ln K\kappa\nu - \frac{\lambda[1 + (\Delta G/\lambda)]^2}{4} \quad (3)$$

corrected for diffusional effects $k_q^{-1} = k_d^{-1} + k_q'^{-1}$,[11] $K = k_d/k_{-d}$, κ is the transmission coefficient, ν is the nuclear frequency, λ is the reorganization energy associated with the inner and outer co-ordination spheres, and ΔG, the standard free-energy change of the reaction, is given by equation (4) for

$$\Delta G(V) = -[E(Os^{VI*}–Os^{V}) - E(Q^{+}–Q)] + w_p - w_r \quad (4)$$

reductive quenching, where w_r and w_p are work terms for bringing the reactants or products to the mean separation for reaction. For weak interactions, the work terms are due only to coulombic attractions and, therefore, are practically zero

Table 3. Rate constants for the quenching of 0.1 mol dm^{-3} *trans*-$[Os(L^1)O_2]^{2+*}$ by a series of aromatic hydrocarbons in degassed acetonitrile at 25 °C

Quencher	$E_p{}^a$/V *vs.* n.h.e.	k_q/dm^3 mol^{-1} s^{-1}	$k_q{}'^b$/dm^3 mol^{-1} s^{-1}	ln k_q'
1,2,4-Trimethoxybenzene	1.36	6.84×10^9	1.04×10^{10}	23.07
1,2,3-Trimethoxybenzene	1.66	3.17×10^9	3.77×10^9	22.05
1,3,5-Trimethoxybenzene	1.73	4.44×10^9	5.71×10^9	22.47
Hexamethylbenzene	1.82	3.52×10^9	4.27×10^9	22.18
Pentamethylbenzene	1.95	3.31×10^9	3.97×10^9	22.10
1,2,4,5-Tetramethylbenzene	2.03	2.89×10^9	3.38×10^9	21.94
1,2,4-Trimethylbenzene	2.13	3.85×10^8	3.93×10^8	19.79
1,2,3-Trimethylbenzene	2.23	9.94×10^7	9.99×10^7	18.42
Mesitylene	2.26	7.81×10^7	7.84×10^7	18.18
p-Xylene	2.30	4.97×10^7	4.98×10^7	17.72
p-Cymene	2.33	3.44×10^7	3.45×10^7	17.36
m-Xylene	2.35	9.22×10^6	9.22×10^6	16.04
Toluene	2.49	5.60×10^5	5.60×10^5	13.24
Cumene	2.56	4.45×10^5	4.45×10^5	13.01
Benzene	2.86	$<10^5$	$<10^5$	<11.51

[a] Ref. 10. [b] k_q' refers to diffusion-corrected value, according to ref. 12.

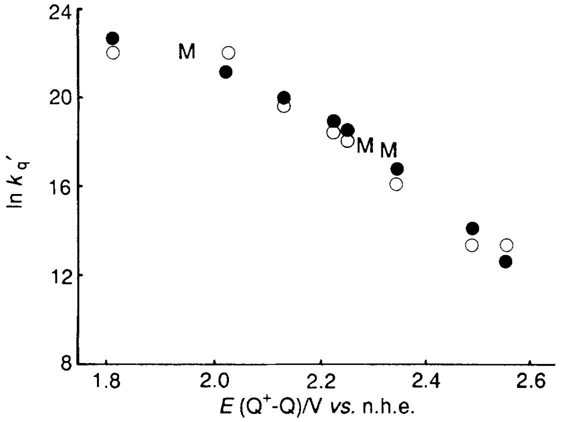

Figure 4. Plot of ln k_q' *versus* $E(Q^+-Q)$ for the electron-transfer quenching of *trans*-$[Os(L^1)O_2]^{2+*}$ by aromatic hydrocarbons in acetonitrile: ○, experimental; ●, theoretical; M = merge

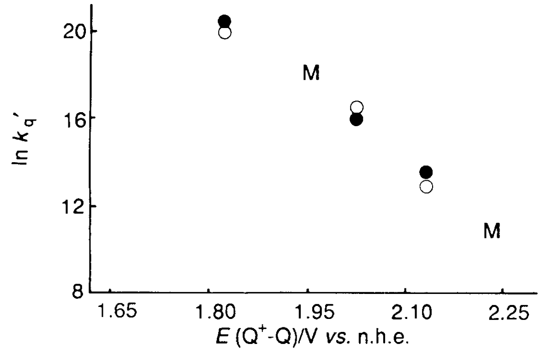

Figure 5. Plot of ln k_q' *versus* $E(Q^+-Q)$ for the electron-transfer quenching of *trans*-$[Os(L^4)O_2]^{2+*}$ by aromatic hydrocarbons in acetonitrile. Symbols as in Figure 4

when at least one of the two reaction partners is uncharged. Thus, the standard free-energy change of the electron-transfer step can simply be taken as equal to the difference in the standard potentials of the two redox couples, *i.e.*, $\Delta G(V) \approx -[E(Os^{VI*}-Os^V) - E(Q^+-Q)]$.

Figure 4 shows the theoretical curve obtained upon fitting of the data in Table 3 by equation (3); the three parameters for the curve fit are $E^\circ(Os^{VI*}-Os^V) = 2.39(10)$ V *vs.* n.h.e., $\lambda = 0.73(05)$ eV, and $RT \ln K\kappa\nu = 0.59(05)$ V *vs.* n.h.e. The excellent agreement of our results with the prediction from Marcus theory suggests that electron transfer is the predominant luminescence quenching mechanism of *trans*-$[Os(L^1)O_2]^{2+*}$ by aromatic hydrocarbons. This is consistent with our prediction that energy transfer does not contribute to a significant extent since the triplet energies of the quenchers are too high for energy transfer to be competitive with electron-transfer reductive quenching. Further evidence for electron-transfer quenching is supported by the observation of a transient signal due to the *p*-dimethoxybenzene cation radical ($\lambda_{max.}$ *ca.* 431 and 456 nm)[13] during the flash photolysis of *trans*-$[Os(L^1)O_2]^{2+}$ and *p*-dimethoxybenzene in degassed acetonitrile. A transient absorption is also observed at *ca.* 460 nm during the flash photolysis of *trans*-$[Os(L^1)O_2]^{2+}$ and 1,2,4-trimethoxybenzene in degassed acetonitrile, possibly attributable to the trimethoxybenzene cation radical. Moreover, the result of $E^\circ(Os^{VI*}-Os^V) = 2.39(10)$ V *vs.* n.h.e. agrees very well with our estimation from spectroscopic and electrochemical data.

Similarly, the phosphorescence of *trans*-$[Os(L^4)O_2]^{2+*}$ is quenched by alkylbenzenes, the rate constants for which are summarized in Table 4. Figure 5 shows the theoretical fit by equation (3) [$E^\circ(Os^{VI*}-Os^V) = 2.00(10)$ V *vs.* n.h.e., $\lambda = 0.60(05)$ eV and $RT \ln K\kappa\nu = 0.62(05)$ V *vs.* n.h.e.]. The lower $E^\circ(Os^{VI*}-Os^V)$ is consistent with our estimation in Table 2.

Effect of Ligand on the Excited-state Redox Properties.—*trans*-Dioxo-osmium(VI) complexes exhibit long-lived triplet excited states, the lifetimes of which are relatively insensitive to the macrocyclic ring size (from L^1 to L^3) and to the nature of the macrocycle (from L^1—L^3 to L^4). The shorter excited-state lifetime of *trans*-$[Os^{VI}(CN)_4O_2]^{2-*}$ may be attributed to the lower rigidity of the equatorial ligands, which provides a more efficient vibrational relaxation mechanism for the excited state, and hence deactivates the phosphorescent pathway. However, no emission is observable both in the solid state and in fluid solution if the equatorial ligands are replaced by primary or secondary amines or π-unsaturated types of ligands as in *trans*-$[Os^{VI}(NH_3)_4O_2]^{2+}$, *trans*-$[Os^{VI}(en)_2O_2]^{2+}$ (en = ethylenediamine), and *trans*-$[Os^{VI}(salen)O_2]$ [salen = ethylenebis(salicylideneiminate)] complexes. The absence of a long-lived excited state for *trans*-$[Os(NH_3)_4O_2]^{2+}$ and *trans*-$[Os(en)_2O_2]^{2+}$ may be ascribed to the existence of intramolecular hydrogen bonding between the Os=O and N–H moieties, which provides an efficient non-radiative relaxation mechanism for the excited states. On the other hand, the π-unsaturated nature of the salen

Table 4. Rate constants for the quenching of 0.1 mol dm^{-3} *trans*-$[\mathrm{Os(L^4)O_2}]^{2+*}$ by a series of aromatic hydrocarbons in degassed acetonitrile at 25 °C

Quencher	E_p[a]/V *vs.* n.h.e.	k_q/dm^3 mol^{-1} s^{-1}	k_q'[b]/dm^3 mol^{-1} s^{-1}	ln k_q'
Hexamethylbenzene	1.82	5.64×10^8	5.80×10^8	20.18
Pentamethylbenzene	1.95	7.55×10^7	7.58×10^7	18.14
1,2,4,5-Tetramethylbenzene	2.03	1.28×10^7	1.28×10^7	16.37
1,2,4-Trimethylbenzene	2.13	3.86×10^5	3.86×10^5	12.86
1,2,3-Trimethylbenzene	2.23	5.44×10^4	5.44×10^4	10.90

[a] Ref. 10. [b] See ref. 12.

ligand would be expected to quench the highly oxidizing $(d_{xy})^1(d_{\pi^*})^1$ state *via* a rapid, internal, reductive quenching mechanism.

The emission energies ($E_{0-0} \approx$ 2.0—2.2 eV) have been found to be relatively insensitive to the nature of the equatorial ligand, in accordance with the emissive state arising from the low-lying spin–orbit B_{1g} and B_{2g} sublevel of the ^3E_g state. The observation of an emission band at similar energies in the d^2-osmium(VI)–nitrido system[2a,b] further supports this formulation. Since the emission energies vary little with ligand variation, the excited-state redox potentials would be expected to parallel the ground-state redox potentials of the complexes. The E°-($\mathrm{Os^{VI}}$–$\mathrm{Os^{V}}$) of *trans*-$[\mathrm{Os(CN)_4O_2}]^{2-}$ is much more negative than that of *trans*-$[\mathrm{Os(L^4)O_2}]^{2+}$ (-0.88 *versus* -0.03 V *vs.* n.h.e.), which is reflected by the quenching rate constants. For example, k_q for the quenching of *trans*-$[\mathrm{Os(L^4)O_2}]^{2+*}$ by triphenylamine is 8.75×10^9 dm^3 mol^{-1} s^{-1} whereas that for the quenching of *trans*-$[\mathrm{Os(CN)_4O_2}]^{2-*}$ is 1.40×10^7 dm^3 mol^{-1} s^{-1} at room temperature. Thus, by simple ligand variation, one could generate a series of photo-oxidants with predictable as well as tunable redox potentials of over 1 V.

The reorganization energy, λ, for the reaction between *trans*-$[\mathrm{Os^{VI}(L)O_2}]^{2+*}$ and alkylbenzenes is *ca.* 0.7 eV. For outer-sphere electron transfer, λ can be regarded simply as the sum of two contributions: $\lambda = \lambda_i + \lambda_o$. The inner-sphere reorganization energy, λ_i, includes both reactants and takes into account the variations in their bond lengths, bond angles, and any specific interactions attendant upon electron transfer. Since the major structural change upon reduction of $\mathrm{Os^{VI*}}$ to $\mathrm{Os^{V}}$ is expected to be in the metal–oxo bond length and *X*-ray studies revealed that the Ru=O distances in the related system only vary slightly from $\mathrm{Ru^{IV}}$ to $\mathrm{Ru^{V}}$ and $\mathrm{Ru^{VI}}$,[14] one would expect no appreciable differences in the bond lengths and angles in *trans*-dioxo-osmium-(VI*) and -(V) as both $\mathrm{Os^{VI*}}$ and $\mathrm{Os^{V}}$ have an electron in the d_{π^*} orbital and converting $\mathrm{Os^{VI*}}$ into $\mathrm{Os^{V}}$ only requires placing an electron into the non-bonding d_{xy} orbital. Thus λ_i can be regarded as negligible for the osmium moiety. However, it is known that benzene undergoes a geometric change arising from the Jahn–Teller distortion in the cation radical which is generated upon electron transfer.[15] An estimate of λ_i for the methylarenes can thus be obtained from the value of the stabilization energy of $\mathrm{C_6H_6}^{\bullet+}$ relative to the hypothetical cation radical in the nuclear configuration of benzene. Such a reorganization energy has been reported by Salem[16] to be *ca.* 2.7 kcal mol^{-1} (0.1 eV). Thus, one would expect that the major contribution to the reorganization energy is λ_0. Since λ_0 would be expected to be similar for structurally related osmium(VI) dioxo complexes of macrocyclic tertiary amines and alkylbenzenes, it is not unreasonable to find that in the quenching studies with alkylbenzenes the λ values for *trans*-$[\mathrm{Os(L^1)O_2}]^{2+*}$ and *trans*-$[\mathrm{Os(L^4)O_2}]^{2+*}$ are similar.

Conclusion

The high excited-state redox potential of *trans*-dioxo-osmium(VI) demonstrates that the excited state is a powerful one-electron oxidant, thereby suggesting the possible application of this complex in generating highly oxidizing species and in photochemical activation of hydrocarbons. Moreover, by ligand variation a series of photo-oxidants with tunable redox potentials could be generated.

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