

Metal-Oxo Photo-oxidants. Photochemistry and Photophysics of *trans*-[Os^{VI}(tmc)(O)₂]²⁺ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) and *trans*-[Os^{VI}(CN)₄(O)₂]²⁻

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trans-[Os^{VI}(tmc)(O)₂]²⁺ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) and *trans*-[Os^{VI}(CN)₄(O)₂]²⁻ are emissive in the solid state and in fluid solutions at room temperature ($\tau \sim 1.0\text{--}1.5 \mu\text{s}$); the ³E_g state of *trans*-[Os^{VI}(tmc)(O)₂]²⁺ is a powerful one-electron oxidant { [Os^{VI}(O)₂]²⁺ + e⁻ → [Os^V(O)₂]⁺, E_f⁰ > 2.0 V vs. normal hydrogen electrode} in aqueous solution, reacting with PPh₃ and (PhCH₂)₂S to give O=PPh₃ and (PhCH₂)₂S=O, respectively.

Relatively few long-lived electronic excited states of metal complexes are powerful oxidants.¹ Although metalloporphyrin and metal-bipyridine complexes are commonly employed as photocatalysts,^{1f,h} these systems suffer from the disadvantage that long-lived excited states with potentials greater than 1.6 V (vs. normal hydrogen electrode, n.h.e.) are difficult to generate, because of the rapid intramolecular reductive quenching that occurs when π -unsaturated ligands are present. We describe here a new class of excited-state reagents that are powerful oxidants (~2 V vs. n.h.e.) in solution at room temperature.^{1c,2}

The optical spectrum of *trans*-[Os^{VI}(tmc)(O)₂][ClO₄]₂³ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) (and [Ph₄As]₂[Os^{VI}(CN)₄(O)₂]⁴ in parentheses) in MeCN displays vibronically structured absorption bands at 312 (320) nm [(d_{xy})² → (d_{xy})¹(d_{π*})¹, ¹A_{1g} → ¹E_g][†] and 355 (370) nm [(d_{xy})² → (d_{xy})¹(d_{π*})¹, ¹A_{1g} → ³E_g][†]. Excitation of *trans*-[Os^{VI}(tmc)(O)₂][ClO₄]₂ or [Ph₄As]₂[Os^{VI}(CN)₄(O)₂] at 350–400 nm results in red emission; photophysical data are summarized in Table 1. The large difference in excitation and emission energies suggests that the emissive state is not E_g (³E_g); it possibly could be either the B_{1g} or B_{2g} sublevel of ³E_g.^{1d,2a,3} Because neither the lifetime nor the intensity of the emission of *trans*-[Os^{VI}(tmc)(O)₂][ClO₄]₂ is quenched by H⁺

(Table 1), the OsO₂²⁺ species can be employed as a photo-oxidant in both protic and aprotic media. The reduction potential (Os^{VI} + e⁻ → Os^V) of [Ph₄As]₂[Os^{VI}(CN)₄(O)₂][‡] is much more negative than that of *trans*-[Os^{VI}(tmc)(O)₂][ClO₄]₂, -1.52 vs. -0.73 V⁵ (vs. cp₂Fe⁺⁰; cp = cyclopentadienyl). Values of the standard reduction potential of the Os^{VI}/Os^V couple (0.01 V vs. n.h.e.)³ and the estimated emission E₀₋₀ (>2 eV)[†] for *trans*-[Os^{VI}(tmc)(O)₂]²⁺ suggest that its ³E_g state [(d_{xy})¹(d_{π*})¹] is an extremely powerful one-electron oxidant: E_f⁰[Os^{VI}(O)₂]²⁺*/[Os^VO₂]⁺ > 2.0 V (vs. n.h.e.) in H₂O (>1.4 V vs. cp₂Fe⁺⁰ in MeCN). The excited-state reduction potential of [Os^{VI}(CN)₄(O)₂]²⁻ is estimated to be ~0.5 V vs. cp₂Fe⁺⁰ in MeCN, assuming its emission E₀₋₀ is ~2 eV.[†] Thus a series of *trans*-dioxo-osmium(vi) photo-oxidants can be obtained by ligand variations.

trans-[Os^{VI}(en)₂(O)₂][PF₆]₂ (en = 1,2-diamineoethane) and *trans*-[Os^{VI}(NH₃)₄(O)₂][PF₆]₂,⁶ whose optical spectra are virtually the same as that of *trans*-[Os^{VI}(tmc)(O)₂]²⁺, exhibited no emission in the solid state or in fluid solution. It is likely that hydrogen bonding between Os=O and N-H groups provides an efficient mechanism for nonradiative decay of the excited states of these complexes.^{2a}

Steady-state quenching results for *trans*-[Os^{VI}(tmc)(O)₂][ClO₄]₂ with substrates are set out in Table 2. The large

[†] d_{π*} = (d_{xz}, d_{yz}); the A_{1g} and E_g symbols are for *trans*-[ML₄(O)₂] complexes with D_{4h} symmetry; see refs. 2(a) and 3. The emission E₀₋₀ was estimated from the emission spectrum. The Os–O stretching frequency in the ³E_g state was estimated from the vibrational spacing in the (d_{xy})² → (d_{xy})¹(d_{π*})¹ transition. See also ref. 2(a).

[‡] The cyclic voltammogram of [Ph₄As]₂[Os^{VI}(CN)₄(O)₂] was obtained in 0.1 M-[Bu₄N]PF₆ acetonitrile solution, working electrode pyrolytic graphite. The Os^{VI}/Os^V couple at -1.52 V vs. cp₂Fe⁺⁰ is quasi-reversible with ΔE_p ~70 mV at a scan rate of 100 mV s⁻¹.

Table 1. Photophysical data for *trans*-[Os^{VI}(tmc)(O)₂][ClO₄]₂ and [Ph₄As]₂[Os^{VI}(CN)₄(O)₂].^a

Complex	Emission ^b λ _{max.} /nm	Lifetime/μs
<i>trans</i> -[Os ^{VI} (tmc)(O) ₂][ClO ₄] ₂	Solid, 630	MeCN, 1.0
	MeCN, 630	H ₂ O, 1.4 0.1 M-CF ₃ CO ₂ H, 1.5
[Ph ₄ As] ₂ [Os ^{VI} (CN) ₄ (O) ₂]	MeCN, 700(br)	MeCN, 0.4

^a The quantum yield of the phosphorescence was $\leq 10^{-3}$ in both cases: standard, quinine sulphate. ^b The emission spectrum was run on a Hitachi 650-60 spectrophotometer.

quenching rate constants ($3-4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for amines are consistent with the substantial driving forces for the one-electron oxidation of NR¹R²R³ to +NR¹R²R³. Flash photolysis of *trans*-[Os^{VI}(tmc)(O)₂]²⁺ and tmpd (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) in degassed acetonitrile yields a transient tmpd⁺ signal (λ_{max.} ~ 600 nm)⁷ that decays by second-order kinetics.

The high reduction potential of *trans*-[Os^{VI}(tmc)(O)₂]²⁺* suggests that the excited-state reagent also can be employed for halide oxidations. Exciplex formation was not observed between *trans*-[Os^{VI}(tmc)(O)₂]²⁺ and X⁻ (X = Cl or Br). The difference in quenching rates of Cl⁻ and Br⁻ (a factor of 100: see Table 2) is parallel with the difference in their oxidation potentials and indicates that the photosystem might be useful for bromide analysis in the presence of chloride.

The Os-O bond in the ³E_g state of *trans*-[Os^{VI}(tmc)(O)₂]²⁺ or [Os^{VI}(CN)₄(O)₂]²⁻ is much weaker than in the ground state [$\nu(\text{Os}=\text{O}): {}^1A_{1g} \sim 870 \text{ cm}^{-1}; {}^3E_g \sim 700 \text{ cm}^{-1}$],[†] implying that these osmium complexes might undergo oxo-transfer photo-reactions.³ Oxygen-atom acceptors (stilbene, phosphine, phosphite, and dialkyl sulphide) quench the phosphorescence of *trans*-[Os^{VI}(tmc)(O)₂]²⁺ at diffusion-limited rates (Table 2). The *k_q* values for *cis*- and *trans*-stilbenes cannot be explained by an energy-transfer mechanism, because the excited-state energy of the osmium complex ($48 \pm 3 \text{ kcal mol}^{-1}$; cal = 4.184 J)[†] is lower than the triplet energy of the organic quencher (*cis*-stilbene, 49; *trans*-stilbene, 57 kcal mol⁻¹).⁸ Although photolysis (λ > 300 nm) of *trans*-[Os^{VI}(tmc)(O)₂]²⁺ and stilbene in degassed MeCN for 3 h produced no epoxide or benzaldehyde, O=PPh₃ and (PhCH₂)₂S=O (yield ~31%) were formed under similar photochemical conditions with PPh₃ and (PhCH₂)₂S. Similarly, O=PPh₃ was formed upon irradiation (λ > 300 nm) of [Ph₄As]₂[Os^{VI}(CN)₄(O)₂] and PPh₃ in MeCN for 3 h. § The phosphorescence of [Os^{VI}(CN)₄(O)₂]²⁻, which has a lower excited-state reduction potential than *trans*-[Os^{VI}(tmc)(O)₂]²⁺, is not efficiently quenched by PPh₃ (*k_q* < 10⁶ dm³ mol⁻¹ s⁻¹). The relative rates of photo-oxidation of PPh₃ by the two Os(O)₂²⁺ complexes suggest that electron transfer to Os(O)₂²⁺* is the initial step in the reaction pathway. The observation that O=PPh₃ is formed in these photoreactions confirms that oxygen-atom transfer⁹ competes effectively with back electron transfer in the photogenerated [Os(O)₂]⁺[PPh₃]⁺ complex.

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§ Steady-state irradiation was performed with a high-pressure mercury short-arc lamp (350 W) equipped with filters or monochromator. Photochemical reaction conditions: *trans*-[Os^{VI}(tmc)(O)₂][PF₆]₂, 6.5 mg; PPh₃, 100 mg; MeCN, 4 ml; *trans*-[Os^{VI}(tmc)(O)₂][PF₆]₂, 20 mg; (PhCH₂)₂S, 30 mg; MeCN, 4 ml. O=PPh₃ was identified by its i.r. band at 1190 cm⁻¹. (PhCH₂)₂S=O was identified by ¹H n.m.r. spectroscopy, δ 3.97 in CDCl₃ with *m*-toluic acid as the internal standard. The yield of (PhCH₂)₂S=O is based on the amount of osmium complex used. No O=PPh₃ or (PhCH₂)₂S=O was formed in the absence of the osmium complex.

Table 2. Rate constants for the quenching of 0.1 M *trans*-[Os^{VI}(tmc)(O)₂]²⁺ in degassed 0.1 M-[Et₄N]ClO₄ acetonitrile solution at 25 °C.

Quencher	<i>k_q</i> ^a /dm ³ mol ⁻¹ s ⁻¹
tmpd	4.4 × 10 ⁹
Ph ₂ NH	3.1 × 10 ⁹
PhNMe ₂	3.5 × 10 ⁹
PPh ₃	4.0 × 10 ⁹
<i>cis</i> -Stilbene	2.1 × 10 ⁹
<i>trans</i> -Stilbene	4.4 × 10 ⁹
(PhO) ₃ P	1.2 × 10 ⁹
Bu ₃ P	7.8 × 10 ⁸
(PhCH ₂) ₂ S	2.2 × 10 ⁸
Et ₂ S	2.4 × 10 ⁸
Thiophene	1.4 × 10 ⁷
NaCl ^b	1.0 × 10 ⁶
NaBr ^b	1.1 × 10 ⁸

^a The second-order quenching rate constants were obtained by both intensity and lifetime-quenching methods. ^b In 0.1 M-CF₃CO₂H.

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