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PHOTOCHEMISTRY AND PHOTOPHYSICS OF *TRANS*-d^2-DIOXO COMPLEXES OF OSMIUM(VI)

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SUMMARY

Trans-$[Os^{VI}(L)(O)_2](ClO_4)_2$ (where L = 14TMC, 15TMC, 16TMC, $CRMe_3$) and *trans*-$[Os^{VI}(CN)_4(O)_2](Ph_4As)_2$ complexes display vibronic structured spin-allowed and spin-forbidden transitions at 300-320 and 345-370nm. The $^3[(d_{xy})^1(d\pi^*)^1]$ excited states of *trans*-dioxoosmium(VI) are emissive and long-lived [lifetimes 0.4 to 1.6μs] both in solid state and in fluid solutions. For *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$, the Os=O bond in the $^3[(d_{xy})^1(d\pi^*)^1]$ state is ca. 0.063Å longer than in the ground state. *Trans*-dioxoosmium(VI) complexes function as a powerful one-electron oxidant with $E(Os^{VI*}/Os^{V})$ ranging from 1.1 to 2.3V vs. N.H.E. Photo-induced oxygen atom transfer reactions have been observed with trialkylphosphines, dialkylsulphides, and alkenes.

INTRODUCTION

The design of luminescent metal complexes with long-lived excited states capable of performing photo-induced atom transfer reactions is an important but relatively new area of research. Previous spectroscopic studies indicated that excitation of metal-oxo complexes at the $d_{xy} \rightarrow d\pi^*$ transition $[d\pi^* = d_{xz}, d_{yz}]$ would produce high energy species with relatively weak metal-oxo bond strength (1-4). It is anticipated that the excited state metal-oxo complexes belong to a new class of compounds from which novel oxygen atom transfer chemistry can be developed. The works of Winkler and Gray on the photophysical properties of *trans*-dioxorhenium(V) complexes (1,2) have aroused our interest in studying the isoelectronic *trans*-d^2-dioxoosmium(VI) species, with the hope of developing powerful metal-oxo photo-oxidants. In view of the presence of rapid internal reductive quenching pathways, inevitably associated with π-unsaturated ligands, which renders the generation of long-lived powerful photo-oxidants (> 1.6V vs. N.H.E.) difficult, a series of σ-saturated macrocyclic tertiary amines are employed as ligands for the synthesis of osmium-oxo complexes. Herein are described the photophysical and photochemical properties of a series of *trans*-d^2-dioxo complexes of osmium(VI) with ligands L = 14TMC, 15TMC, 16TMC, $CRMe_3$, $(CN)_4$ where 14TMC = 1,4,8,11-tetra-

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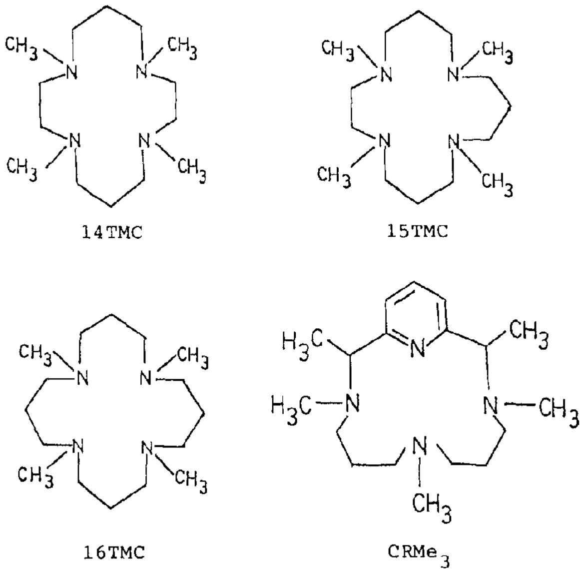
methyl-1,4,8,11-tetraazacyclotetradecane, 15TMC = 1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane, 16TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane, $CRMe_3$ = *meso*-1,2,6,10,11-pentamethyl-2,6,10-triaza[11](2,6)pyridinophane (Figure 1).



14TMC 15TMC

16TMC $CRMe_3$

Fig.1. Structure of macrocyclic tertiary amine ligands.

EXPERIMENTAL SECTION

Reagents and Materials

Sodium chloroosmate(IV) [Na_2OsCl_6] was purchased from Johnson Matthey Chemicals, Ltd. Osmium tetroxide (99.8%) was obtained from Aldrich Chemical Company. The *meso*-1,2,6,10,11-pentamethyl-2,6,10-triaza[11](2,6)pyridinophane ligand ($CRMe_3$) was prepared as previously described(5). Acetonitrile (Mallinckrodt, ChromAR, HPLC grade) was distilled over calcium hydride and potassium permanganate before use. All chemicals and solvents used were of analytical grade.

The osmium complexes were prepared according to the method reported previously (6-8). Organic quenchers were purified according to literature procedures(9).

Physical Measurements and Instrumentation

UV-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. Luminescence quenching experiments were monitored by time-resolved (lifetime) emission measurements, and data were treated by a Stern-Volmer fit as described by $\tau_o/\tau = 1 + k_q\tau_o[Q]$. 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 (10Hz, G-resonator). Luminescence decay signals were recorded either on a Tetronix model 2430 digital oscilloscope or a Tetronix 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 Tetronix digitizers was performed on an Epson PCe IBM-XT compatible personal computer via a GPIB-PC2A interface card, using Tekware GURU II software package for computer control. The waveforms were acquired and analyzed using a program for exponential fits. All solutions for quenching studies were prepared under vacuum in a 10-ml roundbottom flask with a sidearm 1-cm fluorescence cuvette 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.

Steady state irradiation was performed with a high pressure mercury short-arc lamp (350W, Illumination Industries Inc.) equipped with water filter and Corning filters to remove the IR and $\lambda < 330$nm radiations, respectively. Organic products were analyzed by gas chromatograph-mass spectral analyses. All solutions for photochemical experiments were rigorously degassed as in quenching studies.

RESULTS AND DISCUSSION

The electronic absorption spectra of *trans*-d^2-dioxo complexes of osmium(VI) with ligands L = 14TMC, 15TMC, 16TMC, $CRMe_3$, $(CN)_4$ in acetonitrile exhibit vibronically structured absorption bands in the regions 300-320nm and 345-370nm (Figure 2). The UV-visible spectral data are summarized in Table 1. The bands at 300-320nm and 345-370nm are assigned as $(d_{xy})^2 \rightarrow (d_{xy})^1(d\pi^*)^1$ $[^1A_{1g} \rightarrow {}^1E_g]$ and $(d_{xy})^2 \rightarrow (d_{xy})^1(d\pi^*)^1$ $[^1A_{1g} \rightarrow {}^3E_g]$ transitions, respectively, which are vibronically coupled to the $A_{2u}[Os(O)_2]$ stretching mode ($d\pi^* = d_{xz},d_{yz}$). Similar assignments have been reported for the isoelectronic

TABLE 1

UV-visible spectral data of *trans*-$[Os^{VI}(L)(O)_2]^n$ in acetonitrile at 25°C

Complex	λ_{max}/nm (ε_{max}/$M^{-1}cm^{-1}$) $^1A_{1g} \rightarrow {}^1E_g$	 $^1A_{1g} \rightarrow {}^3E_g$
trans-$[Os^{VI}(14TMC)(O)_2]^{2+}$ [a]	312 (1260)	355 (343)
trans-$[Os^{VI}(15TMC)(O)_2]^{2+}$ [a]	307 (1814)	347 (475)
trans-$[Os^{VI}(16TMC)(O)_2]^{2+}$ [a]	306 (1914)	346 (343)
trans-$[Os^{VI}(CRMe_3)(O)_2]^{2+}$ [a]	307 (1934)	365 (367)
trans- $[Os^{VI}(CN)_4(O)_2]^{2-}$	317 (1002)	370 (296)

[a] references (6,10)

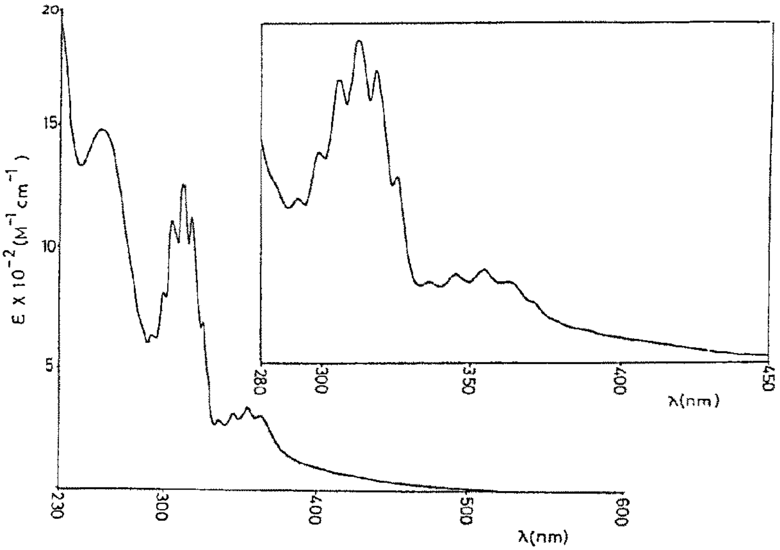


Fig.2. UV-visible spectrum of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ in acetonitrile.

trans-dioxorhenium(V) complexes assuming a D_{4h} symmetry (Figure 3) (1,2). The relative insensitivity of the $(dxy)^2 \rightarrow (dxy)^1(d\pi^*)^1$ transition of the *trans*-dioxoosmium(VI) system to the nature of the equatorial ligand is in accordance with the formulation that the transition occurs within the $d\pi$ orbitals.

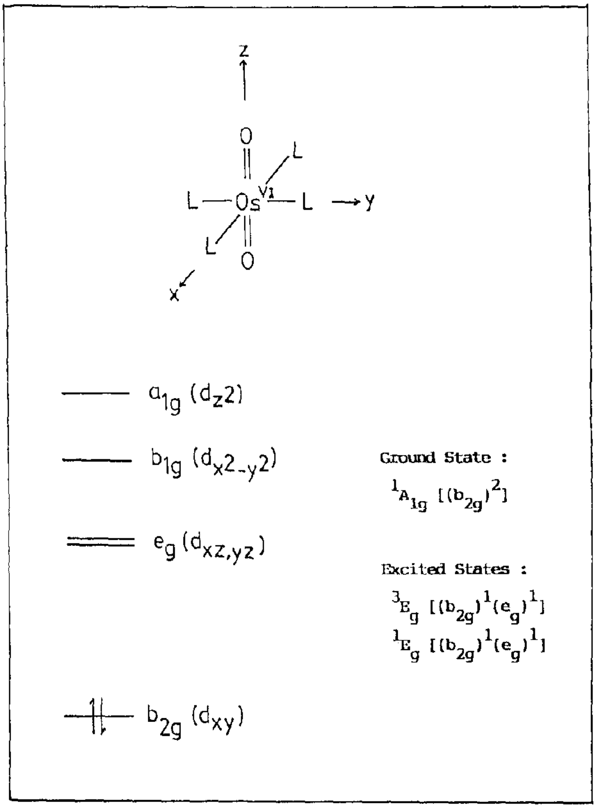


Fig.3. MO diagram showing the d orbital splitting diagram for *trans*-dioxoosmium(VI).

The symmetric osmium-oxo stretching frequencies in the $(dxy)^1(d\pi^*)^1$ excited states of *trans*-dioxoosmium(VI) can be estimated from the vibrational spacing of the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^3E_g$ transition bands. The values are ca. 740-750 cm^{-1}, which are substantially lower than the ground state $\nu_s[Os(O)_2]$ value of 917cm^{-1} [determined by resonance raman spectroscopy], implicating the weakening of the Os=O bond upon light excitation. For *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+*}$, the magnitude of the Os=O bond distortion has been estimated from Franck-Condon fits to the low-temperature absorption spectrum to be 0.063Å (11).

Excitation of *trans*-$[Os^{VI}(L)(O)_2](ClO_4)_2$ (L = 14TMC, 15TMC, 16TMC, $CRMe_3$) and *trans*-$[Os^{VI}(CN)_4(O)_2](Ph_4As)_2$ in the solid state and in fluid solutions at $^1A_{1g} \rightarrow {}^1E_g$ or $^1A_{1g} \rightarrow {}^3E_g$ transition results in red emission (Figure 4). The photophysical data are summarized in Table 2.

TABLE 2

Photophysical data for *trans*-$[Os^{VI}(L)(O)_2]^n$ at room temperature

Complex	Emission λ_{max}/nm	Lifetime/μs
trans-$[Os^{VI}(14TMC)(O)_2]^{2+}$	solid, 620	MeCN,[a] 1.0
	MeCN, 620	H_2O, 1.4
		0.1M CF_3COOH, 1.5
trans-$[Os^{VI}(15TMC)(O)_2]^{2+}$	MeCN, 625	MeCN, 1.0
trans-$[Os^{VI}(16TMC)(O)_2]^{2+}$	MeCN, 600	MeCN, 1.6
trans-$[Os^{VI}(CRMe_3)(O)_2]^{2+}$	MeCN, 710	MeCN, 0.9
trans- $[Os^{VI}(CN)_4(O)_2]^{2-}$	MeCN, 710	MeCN, 0.4

[a] [*trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$] = 0.275mM, 0.1M TEAP as supporting electrolyte.

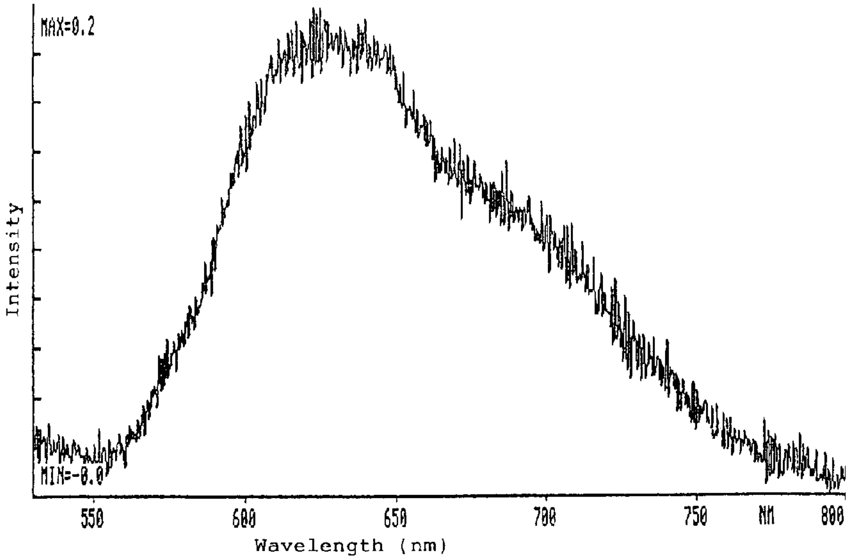


Fig.4. Emission spectrum of a polycrystalline sample of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ at 18K with excitation at 355nm.

The large Stokes shift between the excitation and emission energies suggests that the emissive state is not E_g (^3E_g), but rather it could possibly be derived from the low-lying spin-orbit B_{1g} or B_{2g} sublevel of ^3E_g state(1-3). Unlike the *trans*-dioxotetrakis(pyridine)rhenium(V) complexes(1,2), there is only a small variation in the excited state lifetime of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ in both protic and aprotic solvents, and neither the lifetime nor the intensity of the emission is quenched by proton. This difference in reactivity toward protons could possibly be derived from the fact that the *trans*-dioxorhenium(V) complex would be expected to show a higher affinity for protons than *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$ which possesses a higher positive charge.

The phosphorescence of *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+*}$ is found to display large excited state lifetime dependence on the concentration of *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$ in acetonitrile, with $k_q = 2.6 \times 10^9\ M^{-1}s^{-1}$ over a concentration range of 0.5 to 2.8 mM in 0.1M TEAP (MeCN), suggesting the existence of a self-quenching mechanism. An inherent excited state lifetime of 3.3μs is estimated from a plot of $1/\tau$ versus the concentration of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ (Figure 5). On the contrary, *trans*-$[Os^{VI}(CN)_4(O)_2]^{2-*}$ shows no observable lifetime dependence over a concentration range of 0.7 to 3.6 mM of *trans*-$[Os^{VI}(CN)_4(O)_2]^{2-}$ in 0.1M TEAP (MeCN), suggesting an estimated k_q of $< 10^7\ M^{-1}s^{-1}$ for self-quenching.

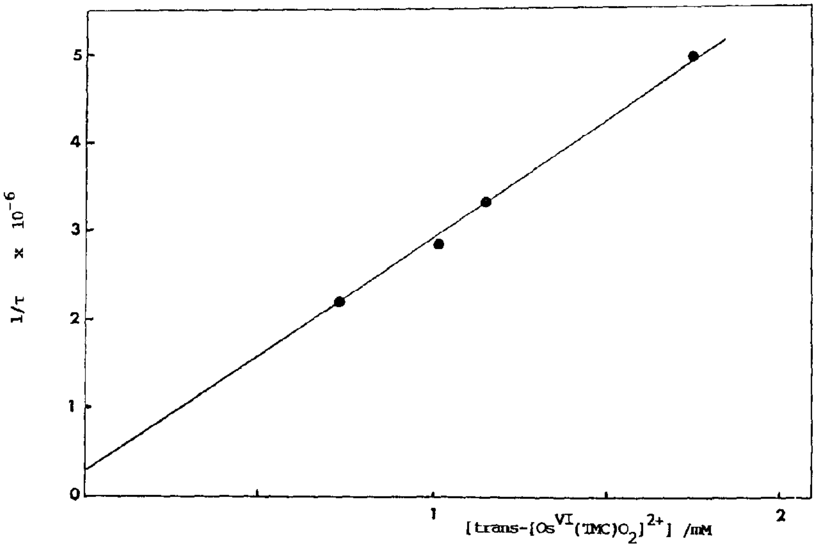


Fig.5. Plot of $1/\tau$ versus the concentration of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ in acetonitrile (0.1M TEAP).

The excited state redox potential $E^{\circ}(Os^{VI*}/Os^{V})$ for *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$ has been determined using spectroscopic and electrochemical data,

$$E^{\circ}(Os^{VI*}/Os^{V}) = E^{\circ}(Os^{VI}/Os^{V}) + E_{o\text{-}o}(Os^{VI}/Os^{VI*}) \qquad (1)$$

where $E_{o\text{-}o}(Os^{VI}/Os^{VI*})$ is the zero-zero spectroscopic energy. Values of the standard reduction potential of the Os^{VI}/Os^{V} couple (0.01V vs. N.H.E. in water) (6) from cyclic voltammetric studies and the estimated emission $E_{o\text{-}o}$ (≃ 2.2eV) for *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+}$ obtained from the low temperature emission spectrum of a solid crystalline sample of *trans*-$[Os^{VI}(14TMC)(O)_2](ClO_4)_2$ at 18K suggest that the ^3E_g state is an extremely powerful one-electron oxidant with $E^{\circ}_f(Os^{VI*}/Os^{V}) \simeq 2.2V$ vs. N.H.E. in water. The excited state redox potentials $E^{\circ}(Os^{VI*}/Os^{V})$ of other *trans*-dioxoosmium(VI) complexes are similarly estimated and are summarized in Table 3.

TABLE 3

Excited state redox potentials of *trans*-$[Os^{VI}(L)(O)_2]^n$ in acetonitrile estimated from spectroscopic data

Complex	$E_{o\text{-}o}$/eV	$E^{\circ}(Os^{VI/V})^a$	$E^{\circ}(Os^{VI*/V})$
		Volt vs. N.H.E.	
trans-$[Os^{VI}(15TMC)(O)_2]^{2+}$	2.2	-0.05	2.15
trans-$[Os^{VI}(16TMC)(O)_2]^{2+}$	2.2	-0.05	2.15
trans-$[Os^{VI}(CRMe_3)(O)_2]^{2+}$	2.0	-0.03	1.97
trans- $[Os^{VI}(CN)_4(O)_2]^{2-}$	2.0	-0.88	1.12

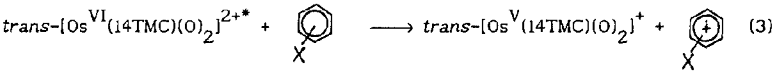
[a]references (3,6,10).

Thus a series of *trans*-dioxoosmium(VI) photo-oxidants with tunable potentials can be obtained by ligand variations.

Given the high excited state redox potentials and the weakening of the metal-oxo bond strength upon light excitation, it is not surprising to find that *trans*-dioxoosmium(VI) functions either as a powerful one-electron oxidant or an oxygen atom transfer reagent in the excited state. Photo-oxidation of aromatic hydrocarbons [RH] to the corresponding cation radicals by *trans*-$[\mathrm{Os^{VI}(14TMC)(O)_2}]^{2+*}$ has been observed (Scheme 1).

SCHEME 1

$$trans\text{-}[\mathrm{Os^{VI}(14TMC)(O)_2}]^{2+} \xrightarrow{h\nu} trans\text{-}[\mathrm{Os^{VI}(14TMC)(O)_2}]^{2+*} \qquad (2)$$



The cation radical from 1,4-dimethoxybenzene was detected by laser flash photolysis [$\lambda_{max} \simeq 431, 456$nm](12) (Figure 6).

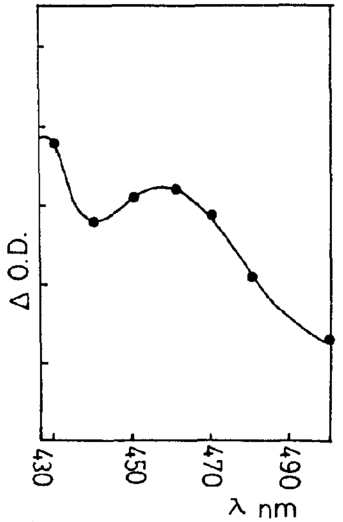


Fig.6. Transient difference spectrum obtained 50μs after flash photolysis of *trans*-$[\mathrm{Os^{VI}(14TMC)(O)_2}](\mathrm{ClO_4})_2$ and 1,4-dimethoxybenzene in degassed acetonitrile.

Steady state photolysis of *trans*-dioxoosmium(VI) complexes at 330-400nm in the presence of trialkylphosphines, dialkylsulphides, and alkenes led to the formation of the corresponding oxygenated products in reasonable yields. The following are representative examples (Scheme 2).

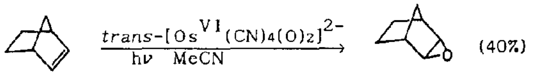
SCHEME 2

$$\textit{trans}\text{-}[\mathrm{Os}^{VI}(14\mathrm{TMC})(\mathrm{O})_2]^{2+} + \mathrm{PPh}_3 \xrightarrow[h\nu]{\mathrm{MeCN}} \textit{trans}\text{-}[\mathrm{Os}^{II}(14\mathrm{TMC})(\mathrm{MeCN})_2]^{2+} + \mathrm{Ph_3P{=}O} \qquad (4)$$

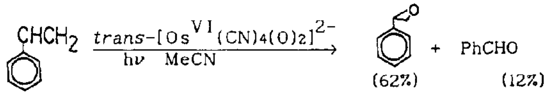
$$\textit{trans}\text{-}[\mathrm{Os}^{VI}(\mathrm{CN})_4(\mathrm{O})_2]^{2-} + \mathrm{PPh}_3 \xrightarrow[h\nu]{\mathrm{MeCN}} \textit{trans}\text{-}[\mathrm{Os}^{II}(\mathrm{CN})_4(\mathrm{PPh}_3)_2]^{2-} + \mathrm{Ph_3P{=}O} \qquad (5)$$

$$(\mathrm{PhCH_2})_2\mathrm{S} \xrightarrow[h\nu\ \ \mathrm{MeCN}]{\textit{trans}\text{-}[\mathrm{Os}^{VI}(\mathrm{CN})_4(\mathrm{O})_2]^{2-}} (\mathrm{PhCH_2})_2\mathrm{S{=}O}\ \ (30\%) \qquad (6)$$

$$(\mathrm{PhCH_2})_2\mathrm{S} \xrightarrow[h\nu\ \ \mathrm{MeCN}]{\textit{trans}\text{-}[\mathrm{Os}^{VI}(14\mathrm{TMC})(\mathrm{O})_2]^{2+}} (\mathrm{PhCH_2})_2\mathrm{S{=}O}\ \ (31\%) \qquad (7)$$



(8)



(9)

The primary steps in these photo-induced oxygen atom transfer reactions have been found to be charge-transfer in nature,

$$\textit{trans}\text{-}[\mathrm{Os}^{VI}(\mathrm{O})_2]^{*} + \mathrm{S} \xrightarrow{k_q} \textit{trans}\text{-}[\mathrm{Os}^{V}(\mathrm{O})_2,\mathrm{S}^{+}] \qquad (10)$$

where S represents an organic substrate. Evidences to support this argument come from the following findings. Firstly, triphenylphosphine quenches the phosphorescence of *trans*-$[\mathrm{Os}^{VI}(14\mathrm{TMC})(\mathrm{O})_2]^{2+*}$ with a rate constant k_q of about 10^2 times faster than that of *trans*-$[\mathrm{Os}^{VI}(\mathrm{CN})_4(\mathrm{O})_2]^{2-*}$. This is in accordance with the much higher excited state redox potential of the former system than the latter. Secondly, linear correlation of $\log(k_q)$ with the vertical ionization potential of alkenes has been found for the *trans*-$[\mathrm{Os}^{VI}(14\mathrm{TMC})(\mathrm{O})_2]^{2+*}$ system (Figure 7), suggesting an electron transfer mechanism occurring in the initial steps of the quenching reactions (Scheme 3).

SCHEME 3

$$[\mathrm{O{=}Os^{VI}{=}O}]^{*} + {>}\mathrm{C{=}C}{<} \xrightarrow{k_q} [\mathrm{O{=}Os^{V}{=}O},\ {>}\overset{+}{\mathrm{C}}\text{-}\overset{\cdot}{\mathrm{C}}{<}\,] \qquad (11)$$

$$[\mathrm{O{=}Os^{V}{=}O},\ {>}\overset{+}{\mathrm{C}}\text{-}\overset{\cdot}{\mathrm{C}}{<}\,] \xrightarrow{k_b} [\mathrm{O{=}Os^{VI}{=}O}] + {>}\mathrm{C{=}C}{<} \qquad (12)$$

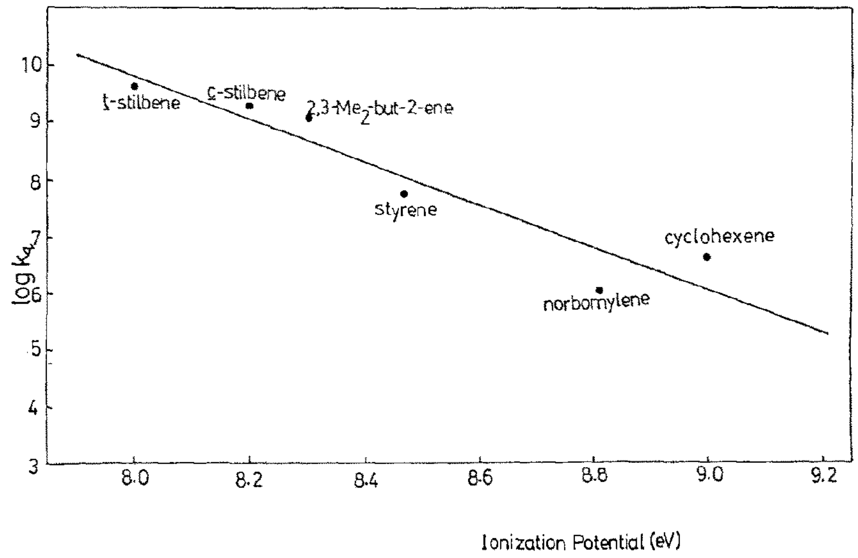


Fig.7. A plot of $\log(k_q)$ versus the vertical ionization potential of alkenes for *trans*-$[Os^{VI}(14TMC)(O)_2]^{2+*}$ in degassed acetonitrile.

CONCLUSION

The *trans*-d^2-dioxoosmium(VI) system, with its high excited state redox potential, shows a strong tendency toward oxidizing organic substrates via an initial electron transfer mechanism. Moreover, with the Os=O bond being weakened in the excited state, they function as potential photo-oxo-transfer reagents. It is envisaged that with the suitable design of metal-oxo complexes, a series of photo-oxidants with tunable reactivities could be generated.

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