At least three independent experiments were conducted at each temperature. The estimated error in the rate constants is 15%.

Pseudo-first-order rate constants are plotted as a function of temperature (Figure 1) and as a function of concentration (Figure 2) through the N_C, N_L, and I phases. On each plot, the experimental values for the phase-transition temperatures determined optically are indicated. The rates of bromination are significantly lower in the N_C phase. Activation energies, enthalpies, and entropies all show pronounced changes through the phase transitions; for example, $\Delta H^{\ddagger}$ = 63, 39, and 12 kcal mol^{-1} for N_L, N_C, and I phases, respectively. However, because of the small temperature ranges accessible, these values are inherently inaccurate. It is clear from these observations that changes in the shape of the aggregate alter the solubilization, orientation, or local motions of guest molecules leading to substantial reactivity changes.

Earlier studies of reactions in lyotropic liquid crystals have reported changes in rate at the liquid crystal–isotropic phase transition.[10–12] Micellar reactions frequently show pronounced changes at the critical micelle concentration.[1,2] The rate control observed in this work is quite different, in that it is specifically associated with changes in shape of the micellar aggregates themselves. Suggested by this work is the intriguing possibility of using micellar shape as a tool in controlling reaction rates and reaction products.

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Registry No. $H_3C(CH_2)_9SO_4Na$, 142-87-0; $H_3C(CH_2)_9OH$, 112-30-1; H_2O, 7732-18-5; (*E*)-$C_6H_5CH{=}CHC_6H_5$, 103-30-0.

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Novel UV–Vis Spectral Feature and Electrochemical Behavior of High-Valent Osmium(VI) Dioxo Complex of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC). Reversible Three-Electron Redox Couple and Vibronic Structured UV–Vis Absorption Bands Involving *trans*-$[Os^{VI}(TMC)O_2]^{2+}$

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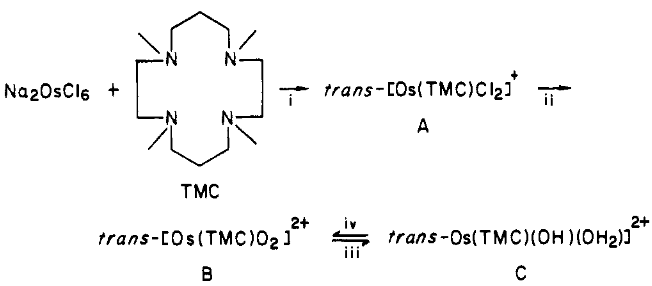
High-valent macrocyclic tertiary amine complexes of Os(VI) have attracted our interests in connection with our work on *trans*-$[Ru^{VI}(TMC)O_2]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[1] Meyer and co-workers[2] recently reported that a reversible three-electron redox couple of Os(VI) to Os(III) was observed with $Os(trpy)(O)_2(OH)^+$ (trpy = 2,2′,2″-terpyridine), using an "activated glassy carbon electrode". This would be a general property of trans Os(VI) dioxo complexes provided that the intermediate Os(V) and Os(IV) species are stable enough with regard to ligand dissociation and μ-oxodimerization ($\text{Os}\overset{\text{O}}{\overline{\quad\quad}}\text{Os}$) processes. We describe here some novel spectroscopic and electrochemical properties of a macrocyclic tertiary amine Os(VI) dioxo complex, *trans*-$[Os^{VI}(TMC)O_2]^{2+}$ (B), that exhibits *a reversible three-electron redox couple at a pyrolytic graphite or glassy carbon electrode.*

Scheme I[a]



[a] (i) Refluxing Na_2OsCl_6, TMC, and tin plates in absolute ethanol. (ii) Oxidation of *trans*-$[Os(TMC)Cl_2]^+$ by 30% H_2O_2. (iii) Electrochemical reduction of B at −0.2 V vs. SCE in 0.1 M $HClO_4$. (iv) Electrochemical oxidation of C at +0.2 V vs. SCE in 0.1 M $HClO_4$.

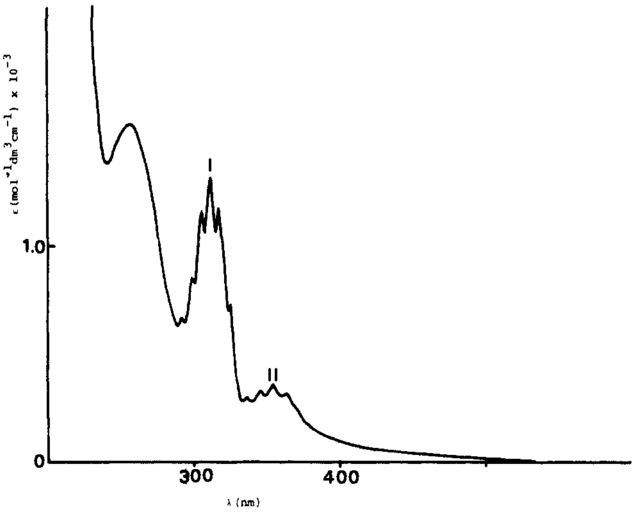


Figure 1. UV–vis absorption spectrum of *trans*-$[Os^{VI}(TMC)O_2]^{2+}$ in CH_3CN.

The synthesis of osmium macrocyclic tertiary amine complexes is outlined in Scheme I (Satisfactory elemental analysis have been obtained for complex A and B). As expected, complex A exhibits an intense UV–vis absorption band at 305 nm characteristic of the $P_\pi(Cl) \rightarrow d_\pi(Os(III))$ charge-transfer transition of *trans*-dichlorotetrammine osmium(III) species.[3] Formulation of the yellow solid B as *trans*-$[Os^{VI}(TMC)O_2](ClO_4)_2$ also comes from its observed diamagnetism ($\mu_{eff} \sim 0\ \mu_B$) and intense IR band at 870 cm^{-1} which is typical of $\nu_{as}(Os{=}O)$ stretch of the $^1A_{1g}$ $[(d_{xy})^2]$ ground state of the trans Os(VI) dioxo species.[4] The UV–vis absorption spectrum of B (Figure 1) in CH_3CN is spectacular, exhibiting two distinct *vibronic structured bands, I and II.* Simple ligand field analysis[5] shows that the lowest energy ligand-field transition from the $^1A_{1g}$ $[(d_{xy})^2]$ ground state to the doubly degenerate d_π (d_{xy}, d_{yz}) level produces ^3E_g $[(d_{xy})^1(d_\pi)^1]$ and ^1E_g $[(d_{xy})^1(d_\pi)^1]$ excited states. Transitions to both excited states are Laporte forbidden and may acquire intensity by vibronic coupling to the A_{2u} $[\nu(Os{=}O)]$ vibrational stretching mode and in the case of a triplet, spin–orbit coupling mechanism. As the spin-allowed transition is more intense than the spin-forbidden one, band I is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition. With the works of Winkler and Gray,[5] strong spin–orbit coupling perturbation will decompose the ^3E_g state into six states of (A_{1g}, A_{2g}), E_g, and (B_{1g}, B_{2g}) symmetries in order of decreasing energy in the D_{4h} double group.

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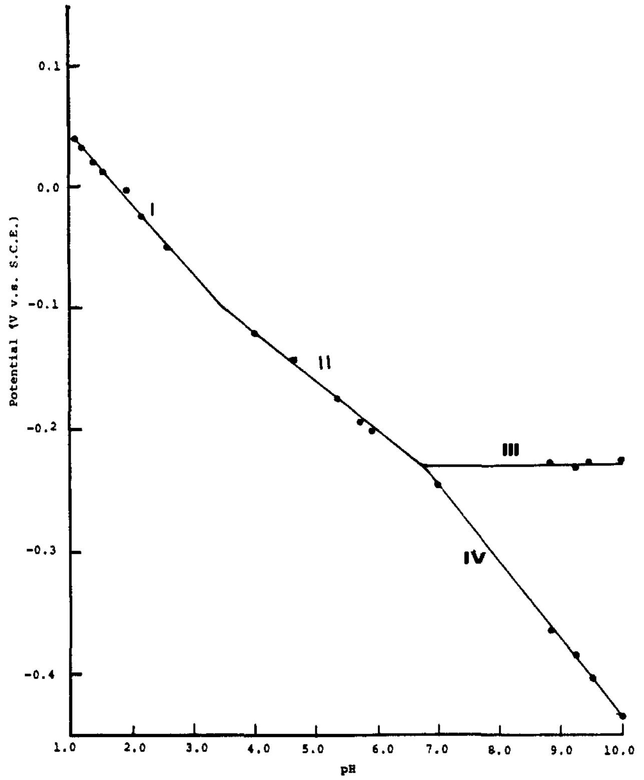

Figure 2. $E_{1/2}$ vs. pH plots for couples I-IV.

Band II may be better considered to arise from the ${}^1A_{1g} \rightarrow E_g({}^3E_g)$ transition, and the $E_g({}^3E_g)$ level acquires singlet character by mixing with the $E_g({}^1E_g)$ state. Very weak absorptions are also observed in the low-energy tail of band II that are possibly attributed to the transitions from ground state to the $B_{1g}({}^3E_g)$ and $B_{2g}({}^3E_g)$ levels. The ν(Os=O) stretcing frequency in the ${}^1E_g$ and ${}^3E_g$ excited state levels (~700-730 cm^{-1}), estimated from the vibrational spacing in band I and II, is substantially smaller than that in the ${}^1A_{1g}$ ground state (870 cm^{-1}), *indicating the weakening of the Os—O bond upon light excitation.*

In aqueous medium (pH 1-6), complex B gave a cyclic voltammogram that showed a reversible three-electron redox wave (*n = 3.00 ± 0.10 by coulometry*). At pH 1.1, the $E_{1/2}$ and ΔE_p (peak-to-peak separation) values for this couple are 0.035 V vs. SCE and 20-30 mV, respectively (scan rate = 50-200 mV/s). The $E_{1/2}$ vs. pH plot is linear (Figure 2) with slopes of -60 and -42 mV at pH ranges of 1-3.2 and 3.2-6.5, respectively. The results indicate that the electrode reaction is, at pH 1-3.2,

$$trans\text{-}[Os^{VI}(TMC)O_2]^{2+} + 3e^- + 3H^+ \rightarrow [Os^{III}(TMC)(OH_2)(OH)]^{2+} \quad (I)$$

at pH 3.2-6

$$trans\text{-}[Os^{VI}(TMC)O_2]^{2+} + 3e^- + 2H^+ \rightarrow trans\text{-}[Os^{III}(TMC)(OH)_2]^+ \quad (II)$$

trans-$[Os^{III}(TMC)(OH_2)(OH)]^{2+}$ (C) has been characterized spectroscopically (λ_{max} ~280 nm) and this can be quantitatively reoxidized (electrochemically or aerially) back to B. The reversibility of couple I is in contrast to the observed electrochemical behavior of *trans*-$[Os^{VI}(en)_2O_2]^{2+}$ (en = 1,2-diaminoethane) and *trans*-$[Os^{VI}(NH_3)_4O_2]^{2+}$. Both of their cyclic voltammograms display irreversible reduction waves.[6] At pH >7, couple I or II splits into two waves corresponding to the following electrode reactions:

$$trans\text{-}[Os^{VI}(TMC)O_2]^{2+} + e^- \rightarrow trans\text{-}[Os^{V}(TMC)O_2]^+ \quad (III)$$

$$trans\text{-}[Os^{V}(TMC)O_2]^{2+} + 2e^- + 2H^+ \rightarrow trans\text{-}[Os^{III}(TMC)(OH)_2]^+ \quad (IV)$$

As expected, *the $E_{1/2}$ value for couple III (-0.225 V vs. SCE) is pH-independent.* For couple IV, the linear $E_{1/2}$ vs. pH plot with slop of -60 mV/pH unit is obtained in agreement with a *two-proton two-electron transfer process* (Figure 2). The direct two-electron reduction from Os(V) to Os(III) indicates that the intermediate Os(IV) oxo species is unstable and undergoes rapid disproportionation in water. This is in contrast to the chemistry of $[Ru^{IV}(TMC)O(OH_2)]^{2+}$ that has been found to be stable in aqueous medium.[1c,7]

The electrochemistry found for B is similar to that of Meyer's work on $[Os^{VI}(trpy)(O)_2(OH)]^+$ except that the latter system is more oxidizing than the former. We note that at pH 1.1, and irreversible reduction wave attributed to the reduction of Os(III) to Os(II) is observed at ~-0.64 V vs. SCE.

Acknowledgment. We acknowledge financial support from the Committee of Conference and Research Grants of University of Hong Kong; Wing-King Cheng is a Croucher Foundation Studentship holder (1984-1987).

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Stereoselective Synthesis of Pikronolide, the Aglycon of the 14-Membered Ring Macrolide Pikromycin, from D-Glucose.[1] Role of MPM and DMPM Protection

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Pikromycin is well-known as the first macrolide antibiotic isolated from an *Actinomyces* by Brockmann and Henkel more than 35 years ago.[2] The total synthesis of its aglycon pikronolide (**1**)[3] as well as pikromycin itself, however, still remains unfinished, mainly because the construction of the β-hydroxy ketone system at the C-3-C-5 of **1** is extremely difficult.[4] Even under mild hydrolytic conditions, pikromycin readily gave the 4,5-anhydro compound kromycin.[4b,5] For the total synthesis of **1** it is very important to overcome such a side reaction, and hence selection of appropriate hydroxyl protecting groups undoubtedly holds the key to success.[4] Recently, we reported highly stereoselective syntheses of methynolide[6] and tylonolide[1] from D-glucose using some stereocontrolled reactions and selective deprotections[7] of benzyl-type [Bn (benzyl),[8] MPM (4-methoxybenzyl),[9] and DMPM (3,4-dimethoxybenzyl)[10]] protecting groups for hydroxy functions at crucial synthetic steps.

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