

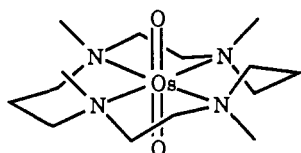
Solvent Dependence of the Reduction Potential of Ground- and Excited-State Redox Couples: *trans*-Dioxo(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclo-tetradecane)osmium(VI/V)

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Recently we reported¹ studies of the excited-state $^*Os^{VI}O_2-$ (TMC)²⁺/ $Os^V O_2$ (TMC)⁺ couple in water. These low-spin d^2 Os(VI) and d^3 Os(V) complexes contain the *trans*-dioxo moiety, with the equatorial ligand sites being filled by the four nitrogen atoms of the tetramethylcyclam (TMC) ligand. Of several possible isomers, the one believed to be the dominant form present¹ is shown as follows:



In the earlier work, we noted possible inconsistencies in the literature estimates^{2,3} for the reduction potentials for the ground- and excited-state $Os^{VI}(TMC)O_2^{2+}/Os^V(TMC)O_2^+$ couples in water and acetonitrile. The excited-state reduction potential (eq 1) may become solvent dependent through the reduction potential

$$E(^*Os^{VI}/Os^V) = E(Os^{VI}/Os^V) + \Delta G(^*Os^{VI}/Os^{VI}) \quad (1)$$

for the ground-state couple ($E(Os^{VI}/Os^V)$), through the solvent dependence of the excitation energy ($\Delta G(^*Os^{VI}/Os^{VI})$) of the excited state, or both. Suspecting that the ground-state couple might be subject to a rather great solvent sensitivity, we have carried out a systematic study, the results of which are reported here.

$[OsO_2(TMC)](PF_6)_2$ was synthesized from $Na_2[OsCl_6]$ and tetramethylcyclam according to the literature.³ Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) were performed with a BAS 100 instrument at 22 ± 2 °C with a (CV) scan rate of 100 mV s^{-1} and (DPV) pulse amplitude (P.A.) -10 to -50 mV and a scan rate of 4 mV s^{-1} . Osteryoung square-wave voltammetry (OSWV) with frequency $5-50 \text{ Hz}$ (4-mV step) was also carried out for several of the solvents. The solutions studied contained 1 mM osmium complex and 0.1 M tetrapropylammonium hexafluorophosphate (TBAH). A conventional H-type cell was used, with glassy carbon, Pt, and SCE as working, counter, and reference electrodes, respectively. For each measurement, a weighed, ca. 3-mg sample of $[OsO_2(TMC)](PF_6)_2$ was added to 3.5 mL of the solvent containing 0.1 M TBAH, and the UV-vis spectrum of the sample was measured. Electrochemical data were collected, and the spectrum of the solution was redetermined. Then the electrochemical measurements were repeated in the presence of ferrocene. In all cases, the solution spectra prior to and following the electrochemical work were in agreement within a few percent.

The Os^{VI}/Os^V couple exhibited quasireversible behavior in all of the solvents examined. The Os^V/Os^{IV} couple was also usually

Table 1. Electrochemical Data as a Function of Solvent

solvent	acceptor no. ^a	$E(Fc^{+/0})$ vs SCE, mV	$E(Os^{VI/V})$ vs $Fc^{+/0}$, V	$E_{pc}(Os^{VI/IV})$ vs SCE, V ^d
water	54.8	(+127) ^b	-0.33 ^e	
methanol	41.3	+324	-0.53 ^f	
<i>N</i> -methylformamide	32.1	+408	-0.69 (90)	-0.61, -1.5
acetonitrile	18.9	+394	-0.70 (70)	-1.49
DMSO	19.3	+403	-0.78 (76)	-1.52
acetone	12.5	+570	-0.74 (60)	-1.26
dimethylformamide	16.0	+493	-0.77 (76)	-1.30
hexamethylphosphoramide	10.6	+600	-0.91 (97)	-1.55

^a Acceptor number values are taken from: Gutmann, V. *Electrochim. Acta* 1976, 21, 661–670. ^b Reported by: Sahami, S.; Weaver, M. J. *Electroanal. Chem.* 1981, 122, 155–170. ^c ΔE_p values are given in parentheses. ^d Position of cathodic peak obtained from cyclic voltammetry with 100 mV/s sweep rate. ^e In aqueous 0.1 M LiTFMS containing 0.02 M borate buffer, pH 9–11. ^f Based on the position of the OSWV peak (the complex is very insoluble in methanol).

detectable at least 1 V negative of the Os^{VI}/Os^V couple but was well-behaved in acetonitrile only.^{1,4} The results are summarized in Table 1.

The values reported for the Os^{VI}/Os^V couple reflect the thermodynamic value; the values of E_{av} ($= (E_{pc} + E_{pa})/2$) from CV agree within $\pm 10 \text{ mV}$ with the peak potentials from OSWV and the value of $E_{1/2}$ ($= E_p + P.A./2$) obtained from DPV. The values recorded for the Os^V/Os^{IV} couple are only approximate.

In several solvents, the CV's of ferrocene were highly irreversible. For example in HMPA, ΔE_p was almost 200 mV with a 100 mV/s sweep rate. However, the values of E_{av} ($= (E_{pc} + E_{pa})/2$) determined for $Fc^{+/0}$ are very similar to those reported by Sahami and Weaver for a 0.1 M $LiClO_4$ medium.⁵ The $Os^{VI}(tmc)O_2^{2+}/Os^V(tmc)O_2^+$ couple was electrochemically much better behaved than $Fc^{+/0}$, typically exhibiting $60-80\text{-mV}$ values of ΔE_p with a 100 mV/s sweep rate. In a few cases, however, the $Os^{VI}(tmc)O_2^{2+}/Os^V(tmc)O_2^+$ couple exhibited only a broad irreversible cathodic wave. Drying of the solution with molecular sieves significantly improved its behavior in about 0.5 h . Results for such solutions are not included here; only those obtained when the experiment was repeated with carefully predried solvent are reported. The extreme water sensitivity of the Os^V/Os^{IV} couple was noted earlier.¹

The reduction potential values for the Os^{VI}/Os^V couple increase (become less negative) as the solvent acceptor number⁶ increases. Data reported for the ruthenium analog⁷ exhibit analogous behavior, as is shown for both metal centers in Figure 1. Thus these couples increase in oxidizing strength as the acceptor number of the solvent increases. Such effects can result from preferential hydrogen bonding of the solvent to the lower oxidation state ($Ru(V)$ or $Os(V)$), and such an interpretation is consistent with the greater basicity of the oxo groups on the V oxidation state (e.g., $pK(Ru^{VI}(tmc)O_2) \sim -1$; $pK(Ru^V(tmc)O_2) \sim 2.8$).⁸

The UV, near-vis spectrum of $Os^{VI}(tmc)O_2^{2+}$ features O-to-Os ligand-to-metal charge-transfer bands at 314 and $260-280 \text{ nm}$ in all of the solvents examined, with the degree of resolution of the vibronic structure of the 314-nm band varying considerably with solvent. The weak absorption to the emissive excited state has not been resolved for the TMC complex. However, for a related complex, the Stokes shift is negligible^{9,10} as might be expected for ground and excited states of this electronic structure. Thus any changes in excited-state energy are expected to be

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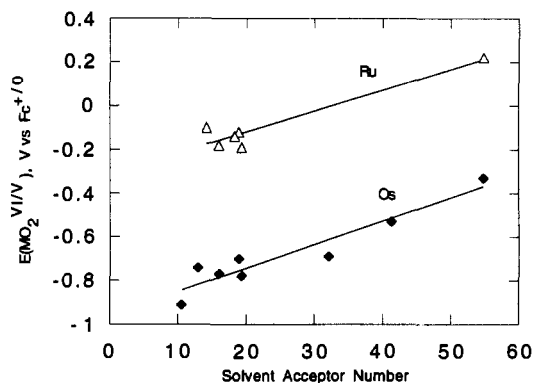


Figure 1. Reduction potential vs the $\text{Fc}^{+/0}$ couple for the $\text{M}^{\text{VI}}(\text{tmc})\text{O}_2^{2+}/\text{M}^{\text{V}}(\text{tmc})\text{O}_2^+$ couple, $\text{M} = \text{Ru}^{\text{II}}$ (open triangles) and $\text{M} = \text{Os}$ (Table 1) as a function of solvent acceptor number. The least-squares slopes of the plots are 0.0095 and 0.011 V/AN, respectively.

reflected in changes in the emission maximum. To test the solvent dependence of the excited-state energy, the emission spectrum was measured in water (acceptor no. 54.8), acetonitrile (18.9), and hexamethylphosphoramide (10.6). Corrected emission maxima (± 3 nm) were 653, 644, and 656 nm, respectively. These very small shifts indicate that the excited-state energy probably does not vary more than 0.05 eV in this solvent series. Thus we conclude that the extreme solvent sensitivity of the reduction potential of the $\text{Os}^{\text{VI}}(\text{tmc})\text{O}_2^{2+}/\text{Os}^{\text{V}}(\text{tmc})\text{O}_2^+$ couple gives rise to a comparable solvent dependence for the $^*\text{Os}^{\text{VI}}(\text{tmc})\text{O}_2^{2+}/$

$\text{Os}^{\text{V}}(\text{tmc})\text{O}_2^+$ couple, with contributions from the solvent dependence of the excitation energy being essentially negligible.

It seems likely that trends such as those reported here will be encountered in other oxo and in nitrido, etc., systems in which hydrogen-bond donation plays an important role in stabilizing the lower oxidation state. The magnitudes of the shifts observed for these dioxo systems, ca. 600 mV over the acceptor number range, may be compared with those previously reported for hexacyanoiron complexes (1300 mV for ground-state reduction potentials),¹¹ pentacarbonyltungsten complexes (~ 500 mV for absorption and emission maxima),¹² and ground-state pentaammineruthenium couples (≥ 500 mV for ground-state reduction potentials).^{13,14} Thus the use of solvent donor/acceptor characteristics can be used for solvent tuning of both ground- and excited-state redox processes.

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