

Table I. Diastereoselectivity of Radical Recombination

	meso-1		(±)-1	
	(±)/meso ^b	% de ^c	(±)/meso ^b	% de ^c
29 °C, <i>hν</i>	0.43 ± 0.1 [3]	40 (meso)	6.23 ± 0.65 [2]	72 (±)
39 °C, <i>hν</i>	0.33 ± 0.07 [1]	50 (meso)	6.05 ± 0.15 [1]	71 (±)
49 °C, <i>hν</i>	0.51 ± 0.06 [1]	32 (meso)		
59 °C, <i>hν</i>	0.59 ± 0.06 [2]	26 (meso)	6.00 ± 0.86 [3]	71 (±)
60 °C	0.78 ± 0.05 [2]	12 (meso)	5.24 ± 0.25 [2]	68 (±)
70 °C	1.09 ± 0.11 [4]	4 (±)	3.74 ± 0.47 [4]	58 (±)
80 °C	1.04 ± 0.11 [3]	2 (±)	1.84 ± 0.46 [2]	30 (±)

^aAll data from decomposition of diazene 1 in DPPC. ^bMean ± standard error; the number of separate experiments on which the mean was based given in brackets. ^cDe = diastereomeric excess with the predominant diastereomer indicated in parentheses.

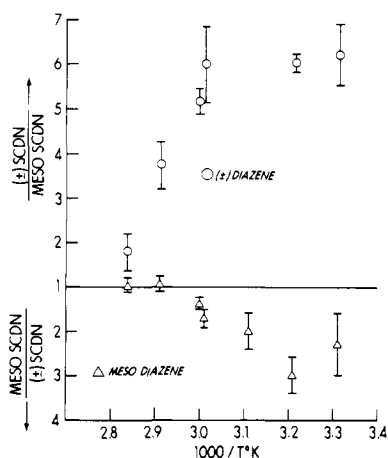


Figure 1. Product ratio for decomposition of (±)- and meso-1 in DPPC multilamellar vesicles. Decomposition is by thermolysis above 59 °C and by photolysis at 59 °C and below.

regard, one might anticipate that diastereoselectivity would be a function of the nature of the molecular aggregate and the position of the reactive pair in the aggregate.

Reversible Three-Electron Redox Couple Based on Os(VI)/Os(III)

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Recent work on polypyridyl-aquo complexes of Ru and Os has shown that stepwise oxidation can occur through a series of oxidation states with the retention of a common coordination number.¹ One of the surprising features about these redox couples is that an extended series of oxidation states can appear over a relatively narrow potential range because of stabilization of the higher oxidation states by proton loss and metal-oxo formation. For example, the couples interrelating Os(II) to Os(VI), through Os(III), Os(IV), and Os(V) in the sequence (bpy)₂Os^{II}(H₂O)₂²⁺ to (bpy)₂Os^{VI}(O)₂²⁺ (bpy is 2,2'-bipyridine) occur over the potential range of 0.16 to 0.78 V vs. SSCE at pH 2.0 (saturated sodium chloride calomel electrode).^{1b} We report here what must represent an extreme case of such behavior; polypyridyl-aquo

(1) (a) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845. (b) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1409. (c) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

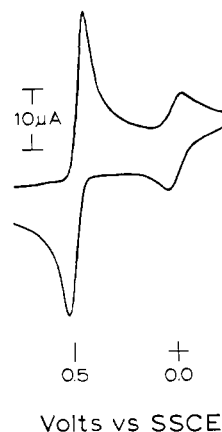


Figure 1. Cyclic voltammogram of 1×10^{-4} M solution of (trpy)Os^{VI}(O)₂(OH)⁺ in 0.1 M HClO₄ (pH 1) at an oxidatively activated Tokai glassy carbon electrode vs. SSCE at 100 mV/s.

complexes of Os in which oxidation states VI to III are interrelated by a three-electron process with all three electrons being gained at the same potential.

The complex [(trpy)Os^{VI}(O)₂(OH)]⁺ was prepared by a route similar to that already described for (phen)Os^{VI}(O)₂(OH)₂ (phen is 1,10-phenanthroline).² The product was purified by dissolution and reprecipitation with ClO₄⁻ from H₂O to give a light tan powder. Characterization of the product included elemental analysis,³ ¹H NMR, and infrared spectroscopy. The ¹H NMR was consistent with a diamagnetic, Os(VI) (d²) system with terpyridine resonances as a doublet at 9.5 ppm, integrating to two protons, a multiplet at 8.7 ppm, integrating to five protons, and a pair of triplets, integrating to two protons each at 8.6 and 8.1 ppm. In the infrared spectrum, the appearance of a single band at 840 cm⁻¹ is consistent with the appearance of the asymmetric stretch of the trans O=Os^{VI}=O group.²

As shown in Figure 1, cyclic voltammetric studies on the Os(VI) salt in water using an oxidatively activated glassy carbon electrode⁴ provide evidence for redox processes at $E_{1/2} = 0.44$ and -0.01 V vs. SSCE, pH 1.0. From the relative peak heights, the wave appearing at the more positive potential appears to be multielectron in nature. Coulometric studies in 0.1 M HClO₄ using a graphite cloth working electrode show that the first reduction wave corresponds to a $n = 3$ (± 0.1) reduction and the second to a $n = 1$ (± 0.08) reduction. Further evidence of a three-electron reduction has been obtained from rotated-disc electrode measurements at a glassy carbon electrode, where the limiting current ratio for the two reduction waves is 3:1. Cyclic voltammetric scan-rate studies of the multielectron wave show that, as the scan rate is decreased from 100 to 10 mV/s, the difference in peak potentials, $\Delta E_p = E_{p,a} - E_{p,c}$, falls from 55 to 26 mV, nearly the theoretical value, $\Delta E_p = 20$ mV, expected for a three-electron wave. Similar studies on the complex (phen)Os^{VI}(O)₂(OH)₂ also show the presence of a three-electron redox couple at $E_{1/2} = 0.39$ V followed by a one-electron reduction at -0.30 V vs. SSCE at pH 1.0, but the three-electron step is less well-defined electrochemically.

The electrochemical observations point to the remarkable fact that, in these coordination environments, Os(VI) is reduced directly

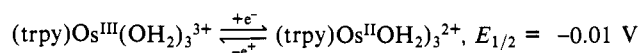
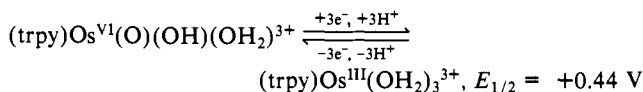
(2) (a) Galas, A. M. R.; Hursthouse, M. B.; Beheman, E. J.; Midden, W. R.; Green, G.; Griffith, W. P. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 194. (b) Chang, C. H.; Midden, W. R.; Deety, J. S.; Beheman, E. J. *Inorg. Chem.* **1979**, *18*, 1364.

(3) Elemental analysis of [(C₁₅H₁₁N₃)Os(O)₂(OH)](ClO₄). Found: C, 31.29; H, 2.12; N, 7.19. Calcd: C, 31.50; H, 2.12; N, 7.35.

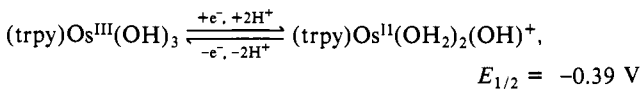
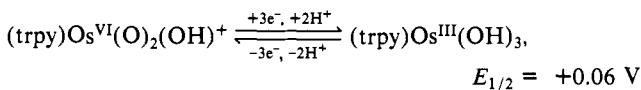
(4) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.*, in press. Activation of the Tokai glassy carbon electrode was accomplished by holding the cell potential at +1.6 V vs. SSCE in 0.1 M HClO₄ for 5 min, followed by two cyclic scans to -0.2 V. This procedure was repeated twice to achieve maximum activation. At a polished, unactivated electrode the waves were much broader and peak to peak separations much larger, 188 mV compared to 55 mV at a sweep rate of 100 mV/s. The surface area of the polished electrode, determined by rotated-disc experiments, was 0.0712 cm².

to Os(III) without intervention of intermediate oxidation states. Although they may be important as kinetic intermediates, Os(V) and Os(IV) are thermodynamically unstable with respect to disproportionation into Os(VI) and Os(III) under these conditions. Phrased another way, the potentials for the Os(V)/(IV) and Os(IV)/(III) couples must occur at more positive potentials than the Os(VI)/(V) couple so that thermodynamically, neither Os(V) nor Os(IV) can build up in solution to a significant degree. The nearly electrochemically reversible behavior observed is remarkable when it is realized, as discussed below, that in the net sense the electrode process involves the transfer of three electrons and of two or even three protons.

The potentials for the Os couples are pH dependent as observed earlier in related couples.¹ At pH 1.0 (0.1 M HClO₄) the redox couples and their $E_{1/2}$ values vs. SSCE are

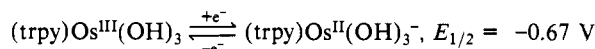
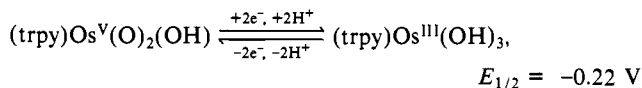
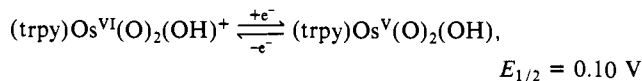


The protonation of the trans-oxo group at pH 1 is evidenced by a shift from $\lambda_{\text{max}} = 355$ to 375 nm in acidic solution which is of the same magnitude as that observed upon protonation of an oxo group in dioxo complexes of Re(V).⁵ At pH 7.0 the redox couples become



(5) Beard, J. H.; Casey, J.; Murmann, R. K. *Inorg. Chem.* **1965**, *4*, 797.

Because of differences in the pH dependences of the couples involved, Os(V) becomes a stable oxidation state past pH 11 and by pH 13.3 the redox couples are



An apt comparison for the Os(VI)/(III) couple is with the well-studied three-electron oxidant HCrO₄⁻ where the intermediate oxidation states Cr(V) and Cr(IV) also appear to be unstable with respect to disproportionation.⁶ However, the Os system shows a dramatically enhanced electrochemical reversibility compared to Cr(VI). An important feature associated with the relative kinetic facility of the Os system may be the retention of a common coordination number through the three oxidation states involved. This feature may also play an important role in the ability of related systems to act as redox catalysts.⁷

Acknowledgment. We thank the National Science Foundation (NSF) under Grant CHE-8304230 and National Institution of Health (NIH) under Grant 1-R01-GM32296-01 for support of this research.

(6) (a) Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347. (b) Miller, I. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1967**, *15*, 49. (c) Miller, F. J.; Zittel, H. E. *J. Electroanal. Chem.* **1964**, *7*, 116.

(7) (a) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.*, submitted for publication. (b) Gersten, S. W.; Samuels, G. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029. (c) Ellis, C. D.; Gilbert, J. A.; Murphy, W. R., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4842. (d) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1326. (e) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C.

Additions and Corrections

Syntheses of Heme *d* Models [*J. Am. Chem. Soc.* **1984**, *106*, 5746–5748]. KEVIN M. SMITH* and JAN-JI LAI

Page 5746; the second sentence of the first paragraph should read: Examples include siroheme,¹ probably the heme in sulfhemoglobin,² and...

Page 5747, Figure 1 caption should read: High-pressure liquid chromatogram of the mixture of chlorin dimethyl esters **12–15**.²⁰

Biosynthesis of Polyprenols in Higher Plants. The Elimination of the *pro*-4S Hydrogen Atom of Mevalonic Acid during the Formation of Their (*Z*)-Isoprene Chain [*J. Am. Chem. Soc.* **1983**, *105*, 6178–6179]. TAKAYUKI SUGA,* TOSHIFUMI HIRATA, TADASHI AOKI, and TSUYOSHI SHISHIBORI

Page 6178, line 5: we commented that no example contravening Cornforth's stereochemical picture for the biosynthesis of isoprenoids¹ has yet been found. However, we inadvertently lost sight of referring that the hydrogen elimination opposed to this picture had been observed in the formation of nerol^{2–4} and (2*Z*,6*E*)-farnesol.²

(1) In addition to ref 3–5 in our previous communication, refer to: Popjak, G.; Cornforth, J. W. *Biochem. J.* **1966**, *101*, 553–568.

(2) Jedlicki, E.; Jacob, G.; Faini, F.; Cori, O.; Bunton, C. A. *Arch. Biochem. Biophys.* **1972**, *152*, 590–596.

(3) Banthorpe, D. V.; Le Patourel, G. N. J.; Francis, M. J. O. *Biochem. J.* **1972**, *130*, 1045–1054.

(4) Banthorpe, D. V.; Ekundayo, O.; Rowan, M. G. *Pytochemistry* **1978**, *17*, 1111–1114.

Free Energy Relationship for Electron Transfer Far from Equilibrium. Analysis of Reversibility in the Endergonic Region [*J. Am. Chem. Soc.* **1982**, *104*, 4186]. R. J. KLINGLER and J. K. KOCHI*

Page 4190, third paragraph: The pair of sentences beginning with: Second, the applicability... should be deleted. The next two sentences should read—Second, the Marcus, the Rehm–Weller, and the Marcus–Levine–Agmon relationships are equally applicable over the entire experimental free energy change. All three relationships yield values of ΔG_0^\ddagger that deviate less than 0.3 kcal mol⁻¹ only at the extrema.

This change is necessitated by the discovery of a typographical error in the computer program used to perform the computations resulting in Figure 5a, which is correctly given below. Our re-examination of this figure was stimulated by Dr. J. R. Murdoch.

