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 $HClO_4$) the redox couples and their $E_{1/2}$ values vs. SSCE are

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{VI}}(\mathrm{O})(\mathrm{OH})(\mathrm{OH_2})^{3+} \underset{-3e^-,\ -3H^+}{\overset{+3e^-,\ +3H^+}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{III}}(\mathrm{OH_2})_3{}^{3+},\ E_{1/2} = +0.44\ \mathrm{V}$$

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{III}}(\mathrm{OH_2})_3{}^{3+} \underset{-e^+}{\overset{+e^-}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{II}}\mathrm{OH_2})_3{}^{2+},\ E_{1/2} = -0.01\ \mathrm{V}$$

The protonation of the trans-oxo group at pH 1 is evidenced by a shift from $\lambda_{max} = 355$ 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

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{VI}}(\mathrm{O})_2(\mathrm{OH})^+ \underset{-3e^-,\ -2H^+}{\overset{+3e^-,\ +2H^+}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{III}}(\mathrm{OH})_3,\quad E_{1/2} = +0.06\ \mathrm{V}$$

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{III}}(\mathrm{OH})_3 \underset{-e^-,\ -2H^+}{\overset{+e^-,\ +2H^+}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{II}}(\mathrm{OH_2})_2(\mathrm{OH})^+,\quad E_{1/2} = -0.39\ \mathrm{V}$$

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

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{VI}}(\mathrm{O})_2(\mathrm{OH})^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{V}}(\mathrm{O})_2(\mathrm{OH}),\quad E_{1/2} = 0.10\ \mathrm{V}$$

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{V}}(\mathrm{O})_2(\mathrm{OH}) \underset{-2e^-,\ -2H^+}{\overset{+2e^-,\ +2H^+}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{III}}(\mathrm{OH})_3,\quad E_{1/2} = -0.22\ \mathrm{V}$$

$$(\mathrm{trpy})\mathrm{Os}^{\mathrm{III}}(\mathrm{OH})_3 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (\mathrm{trpy})\mathrm{Os}^{\mathrm{II}}(\mathrm{OH})_3{}^-,\ E_{1/2} = -0.67\ \mathrm{V}$$

An apt comparison for the Os(VI)/(III) couple is with the well-studied three-electron oxidant $HCrO_4^-$ 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]

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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]

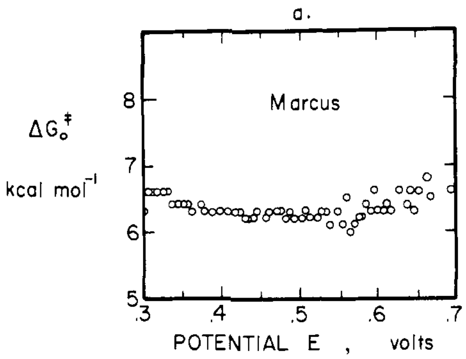
Biosynthesis of Polyprenols in Higher Plants. The Elimination of the *pro*-4*S* Hydrogen Atom of Mevalonic Acid during the Formation of Their (*Z*)-Isoprene Chain [*J. Am. Chem. Soc.* **1983**, *105*, 6178–6179]. TAKAYUKI SUGA,* TOSHIFUMI HIRATA, TADASHI AOKI, and TSUYOSHI SHISHIBORI

Page 6178, line 5: we commented that no example contravening Cornforth's stereochemical picture for the biosynthesis of isoprenoids[1] 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]

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 $\Delta G_0^\ddagger$ 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 reexamination of this figure was stimulated by Dr. J. R. Murdoch.



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

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