Inorg. Chem. **1992**, *31*, 3879–3881

Multielectron-Transfer Kinetics for *cis-* versus *trans-*Dioxorhenium(V) Species: Isoelectronic Modeling with Osmium(VI/V) and Control of Interfacial Reactivity by Rhenium(IV) Accessibility

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Received June 4, 1992

As part of a broader effort aimed at understanding the kinetics of multielectron-transfer processes, especially at electrochemical interfaces, we have been exploring the chemistry of dioxorhenium(V) species.[1–3] With pyridyl (py) or bipyridyl (bpy) moieties as ancillary ligands, these species are oxidizable by one electron,[1a,b,2h] and reducible by two or even three electrons with uptake of an equivalent number of protons,[1a,b,2h] e.g.:[4]

$$trans\text{-}(O)_2Re^{V}(py)_4^{+} + 2e^{-} + 2H^{+} \rightarrow trans\text{-}(OH)_2Re^{III}(py)_4^{+} \quad (1a)$$

$$cis\text{-}(O)_2Re^{V}(bpy)(py)_2^{+} + 2e^{-} + 2H^{+} \rightarrow cis\text{-}(OH)_2Re^{III}(bpy)(py)_2^{+} \quad (1b)$$

In an earlier report on the synthesis, spectroscopy, and electrochemical thermodynamics of the first cis complexes, we noted qualitatively (single-sweep-rate cyclic voltammetry peak separation measurements) that the *kinetic* reversibility of reaction 1b is much greater than that of reaction 1a.[1a] We further suggested that the reactivity difference could be due, in part, to differences in thermodynamic accessibility for the kinetic intermediate state, Re(IV).[1a] We now wish to report in preliminary detail (1) the mechanisms for electrochemical reduction of *cis-* and *trans-*dioxorhenium(V) species in acidic and neutral solutions and (2) quantitative measures of the electrochemical exchange kinetics at near-neutral pH*.[5] From (1) and (2) we indeed find that access to Re(IV) is an important factor in differentiating cis/trans electrochemical kinetics and, further, that a semiquantitative reactivity analysis is possible based on comparisons to isoelectronic osmium species.

Potential-dependent rate constants, $k(E)$, for electrochemical reduction of dioxorhenium(V) at a carbon fiber[6] microelectrode surface (10-μm diameter) were readily obtained from mass-transport-corrected and back-reaction-corrected[7] steady-state currents, i_{cor}, via eq 2,[8] where n is the total of electrons transferred,

$$k(E) = i_{cor}/nFAc \quad (2)$$

F is the Faraday constant, A is the electrode area, and c is the solution concentration of the reactant. Standard (or electrochemical exchange) rate constants, k_s, were obtained by extrapolation to the appropriate formal potential, E_f (where E_f was obtained by averaging cyclic voltammetry peak potentials in the limit of zero sweep rate). At pH* = 6, the k_s values are 1.1×10^{-3} cm s^{-1} for cis-$(O)_2Re^{V}(bpy)(py)_2^{+}/(OH)_2Re^{III}(bpy)(py)_2^{+}$ and 9.5×10^{-6} cm s^{-1} for $trans$-$(O)_2Re^{V}(py)_4^{+}/(OH)_2Re^{III}(py)_4^{+}$. Both rate constants are concentration independent, demonstrating that disproportionation pathways are kinetically unimportant. The potential dependencies of the rate constants lead to transfer coefficients (or electrochemical Brönsted coefficients[8,9]) of 0.47 and 0.32 for reactions 1a and 1b, respectively (both at pH* = 6). These values are close to 0.5, implying (in both cases) a reaction order in electrons of 1[9] and, therefore, overall rate control[8a,c] via Re(V → IV) reduction. Additional measurements as a function of pH* in the range from 1 to 8 yielded reaction orders in protons of 1 and 0,[10] respectively, for the trans and cis forms. Thus the rate-determining steps are[11]

$$trans\text{-}(O)(OH)Re^{V}(py)_4^{2+} + e^{-}(electrode) \rightarrow trans\text{-}(O)(OH)Re^{IV}(py)_4^{+} \quad (3)$$

$$cis\text{-}(O)_2Re^{V}(bpy)(py)_2^{+} + e^{-}(electrode) \rightarrow cis\text{-}(O)_2Re^{IV}(bpy)(py)_2^{0} \quad (4)$$

Given the commonality of rate-determining *redox* steps, we suggest again that differences in thermodynamic accessibility to Re(IV) from Re(V) may well account for much of the ca. 120-

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[1] (a) Ram, M. S.; Johnson, C. S.; Blackbourn, R. L.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 238. (b) Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y.-H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928. (c) Blackbourn, R. L.; Jones, L. M.; Ram, M. S.; Sabat, M.; Hupp, J. T. *Inorg. Chem.* **1990**, *21*, 1791. (d) Ram, M. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 130. (e) Johnson, C. S.; Mottley, C. S.; Hupp, J. T.; Danzer, G. I. *Inorg. Chem.*, submitted for publication (Raman studies).

[2] Related reports on dioxorhenium chemistry: (a) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373. (b) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346. (c) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889. (d) Brewer, J. C.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 3334. (e) Thorp, H. H.; Kumar, C. V.; Turro, N. J.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 4364. (f) Newsham, M. D.; Giannelis, E. P.; Pinnavia, T. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 3885. (g) Brewer, J. C.; Gray, H. B. *Reprints: Symposium on Selective Catalytic Oxidation of Hydrocarbons, ACS Division of Petroleum Chemistry*; American Chemical Society: Washington, DC, 1990; pp 187–191. (h) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256.

[3] Early synthetic and structural reports: (a) Beard, J. H.; Calhoun, C.; Casey, J.; Murmann, R. K. *J. Am. Chem. Soc.* **1968**, *90*, 3389. (b) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B* **1978**, *B34*, 923. (c) Bear, J. H.; Murmann, R. K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2467. (d) Murmann, R. K. *Inorg. Synth.* **1968**, *8*, 173. (e) Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1971**, *10*, 2352. (f) Fenn, R. H.; Graham, A. J.; Johnson, N. P. *J. Chem. Soc. A* **1971**, 2880. (g) Beard, J. H.; Casey, J.; Murmann, R. K. *Inorg. Chem.* **1965**, *4*, 797.

[4] The doubly protonated Re(III) species could, in principle, be represented as aquo–oxo complexes.

[5] Acetonitrile/water mixtures were employed as described previously[1a,b] to enhance solubility. Apparent pH's, designated pH*, were maintained with buffers of ~0.1 M ionic strength and measured with a glass combination electrode.

[6] Carbon fibers were employed in place of platinum or gold because of anticipated interferences from hydrogen evolution, especially with the trans complex.

[7] Back-reaction corrections were negligible for all but the highest pH *cis*-dioxo measurements.

[8] (a) Albery, W. J. *Electrode Kinetics*; Clarendon Press: London, 1975. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980. (c) Vetter, K. J. *Electrochemical Kinetics*; Academic Press: New York, 1967.

[9] Ram, M. S.; Hupp, J. T. *J. Phys. Chem.* **1990**, *94*, 2378.

[10] Proton reaction orders were derived from variable-pH rate measurements at fixed absolute electrochemical potential, rather than fixed overpotential. (See ref 6c for further discussion.) Above pH* = 7–8, a change in *electron* reaction order seems to occur for both the cis and trans species.

[11] In an earlier report[1b] we suggested, on the basis of a qualitative analysis of cyclic voltammogram (CV) shapes, that Re(IV → III) might be rate determining. The discrepancy with the quantitative measurements here could be due to (1) differences in reaction medium (MeOH/water vs CH_3CN/water), (2) differences in pH* (see footnote 10), (3) distortions in CV shapes due to overlap with Re(III/II), and/or (4) in the case of the cis complex, possible partial decomposition of the Re(II) form during slow voltammetric cycling (L. M. Jones-Skeens, unpublished work).

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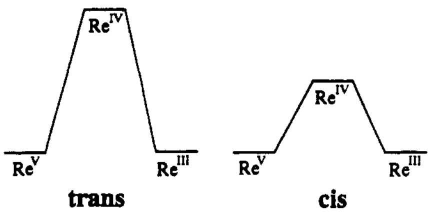

Figure 1. Schematic representation of cis versus trans dioxorhenium energetics for oxidation states V, IV, and III at E_f(V/III).

fold difference in cis vs trans reduction rates (see Figure 1). The proposed Re(IV) accessibility effects could, of course, be quantified if formal potentials for the two Re(V/IV) couples could be determined in relation to the overall V/III potentials. In both cases, however, E_f(V/IV) necessarily lies more negative than both E_f(IV/III) and E_f(V/III), rendering it (the V/IV potential) inaccessible by conventional methods.

Despite these difficulties, *relative* Re(V/IV) potentials can be inferred in an approximate fashion by consideration of isoelectronic, and nearly isostructural, Os(VI/V) redox couples. Comparative measurements by Dobson et al.[12] of *cis*- and *trans*-$(O)_2Os(bpy)_2^{2+}$ reduction show, first, that Os(VI/V) (analogous to Re(V/IV)) is directly observable by cyclic voltammetry and, second, that the cis and trans potentials differ by 370 mV versus a common reference electrode (cis is more positive). We will assume that a similar difference exists for the isoelectronic Re(V/IV) couples. Our real interest, however, is not in the absolute cis/trans Re(V/IV) potential difference but in the potential difference relative to the appropriate V/III potentials. The latter already differ by +184 mV at pH* = 6 (cis minus trans), implying that the corresponding V/IV potentials will differ by ca. 186 mV when referenced separately to the appropriate two-electron potentials.[13,14] (In other words, the Re(V/IV) trans couple is considerably *less* accessible than the cis thermodynamically, under two-electron-exchange conditions (i.e. at E_f(V/III)).)

To assess the consequences in terms of two-electron-transfer rates, it is sufficient to note that for the mechanisms invoked (eqs 3 and 4), plots of log k(V/III) vs potential (i.e. electrochemical linear free energy plots or Tafel plots[8]) are necessarily equivalent to plots of log ($2k$(V/IV)) vs potential for the same compounds. Representative plots are shown in Figure 2. (Note that the potential axes are arranged to facilitate rate comparisons at common overpotentials (two electron) rather than at common absolute potentials.) Because reduction rates necessarily increase as the electrode potential is made more negative and because E_f(V/IV) is necessarily more negative (for both complexes) than E_f(V/III), rate measurements at E_f(V/III) will necessarily be endoergonic with respect to the rate-determining V → IV steps and the rates themselves will necessarily be diminished from the values they would take at the V/IV formal potentials. Note further that because of the estimated 186-mV difference in relative cis and trans V/IV potentials (see above), rate diminution (at E_f(V/III)) will be greater for the trans reduction. A quantitative estimate of the relative diminution effect can be made via the Butler–Volmer equation

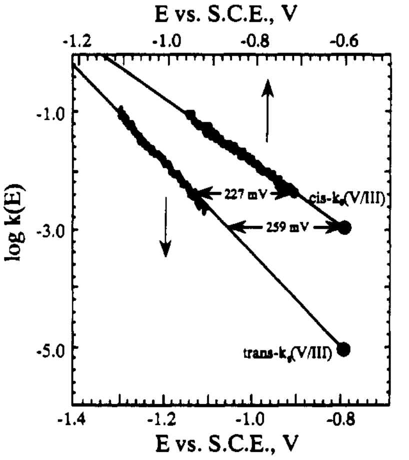

Figure 2. Plots of log k(V/III) versus potential for *cis*-$(O)_2Re(bpy)(py)_2^+$ and *trans*-$(O)_2Re(py)_4^+$ reduction at pH* = 6 in 50:50 (v/v) acetonitrile/water. The working electrode is a carbon fiber, and potentials are referenced to saturated calomel. Under these conditions, E_f(cis) = −605 mV and E_f(trans) = −790 mV.

$$k(E) = k_s \exp(-\alpha F(E - E_f)/RT) \qquad (5)$$

where α is the transfer coefficient. For *cis*- and *trans*-dioxorhenium, the 186-mV difference in relative E_f(V/IV)'s would translate into a 30-fold difference in rate constants (cis vs trans; both one- and two-electron rates) when evaluated at the respective E_f(V/III)'s.[14,15] Thus the majority of the observed reactivity difference can be rationalized by the accessibility argument.

Alternatively, one could assume that cis/trans reaction rates are equal at the respective E_f(V/IV)'s and then calculate (via eq 5) the relative E_f(V/IV) potential difference[16] needed to obtain the observed cis/trans difference in two-electron standard rates. While the calculation is straightforward, there is a subtlety due to the slight difference in transfer coefficients (or unitless log k vs E slopes; see eq 5 and Figure 2) for the two rate processes. The calculation then becomes dependent also on the *absolute* potentials chosen. For example, if E_f(V/IV)(cis) is assumed to be as negative as (but not more negative than) E_f(V/III)(cis), then the relative difference in E_v(V/IV) potentials is calculated as +259 mV. On the other hand, if E_f(V/IV)(cis) is taken to be, e.g., 100 mV more negative than E_f(V/III)(cis), then the calculated potential difference becomes +227 mV. In either case, reasonable agreement is found with the isoelectronic modeling estimate (+186 mV), supporting our contention that Re(IV) accessibility differences are largely responsible for the two-electron, two-proton cis vs trans reactivity difference.

Finally, it is worth noting that while the cis/trans rate analysis relies upon a comparison of isoelectronic osmium for quantitative formulation, it also follows in a qualitative fashion from straightforward electronic structure considerations.[17] For d^2 metal–dioxo complexes in general, a strong thermodynamic preference exists for the trans isomer over the cis.[17,18] The preference is based on the ability of the former to confine both available valence electrons to a single d orbital (d_{xy}) which is

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(12) Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2357.

(13) It could be argued that an even better comparison of relative d^3(Re) accessibilities would be cis [E_f^{Os}(VI/V) − E_f^{Os}(V/IV)] versus trans [E_f^{Os}(VI/V) − E_f^{Os}(V/IV)]. For the cis complex at pH = 6 the difference is +200 mV.[12] For the trans complex there is a difficulty in that the Os(IV) state is not accessible (i.e., Os(IV) is unstable with respect to disproportionation to Os(III) and Os(V)). An upper limit estimate for E_f^{Os}(VI/IV), however, is provided by E_f^{Os}(VI/III), which *is* accessible.[12] This yields a lower limit estimate of −80 mV for the difference in one- and two-electron trans potentials and ultimately an *upper* limit estimate of 280 mV for the relative difference in cis vs trans Os(V) (or, by inference, Re(IV)) accessibility at the respective two-electron formal potentials.

(14) Since the inferred E_f(V/IV) values are for pH-independent rhenium redox reactions, one would ideally like to compare them to pH-independent rate processes. Unfortunately, the cis and trans mechanisms differ in that the latter involves Re(V) preprotonation (see eqs 3 and 4 and text). Evidently, the trans pathway involving initial direct reduction of Re^V (i.e. no preprotonation) is even slower. The observed rate ratio of 115 represents, then, only a lower limit estimate for the reactivity difference for cis vs trans reduction via a common pH-independent mechanistic pathway.

(15) Alternatively, the ca. 280-mV difference suggested in ref 13 would yield a k_s(V/III) cis:trans ratio of 170.

(16) "Relative" here signifies E_f(V/IV) values versus the appropriate E_f(V/III) values (as discussed above), rather than versus an external reference electrode.

(17) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(18) See, for example, ref 12 and: Dobson, J. C.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3283.

geometrically orthogonal to the rhenium–oxo core.[17,19] For the cis case, on the other hand, the one filled metal d orbital unavoidably interacts (unfavorably) with filled $p\pi^*$ oxygen orbitals, thereby destabilizing the complex. For d^3 and d^4 configurations, on the other hand, higher-lying orbitals are occupied and the special stability of the trans isomer is diminished or absent. In a redox sense, the special stability of d^2 trans renders it resistant to reduction. If the corresponding d^3/d^4 formal potential is less affected by isomeric interconversion, and if that potential is moved sufficiently far positive (by coupling ET to proton uptake), then d^3 will be thermodynamically inaccessible in both cases, but more inaccessible for the trans form. All else being equal, the trans isomer should display the slower overall two-electron-transfer kinetics, provided that the $d^2 \rightarrow d^3$ step is rate determining.

Acknowledgment. We thank the Office of Naval Research for support of this work. J.T.H. also acknowledges a Dreyfus Teacher-Scholar Award (1991–6) and a fellowship from the Alfred P. Sloan Foundation (1990–2).

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(19) Mingos, D. M. P. *Organomet. Chem.* **1979**, *179*, C29.