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The Role of Statistics in the Electrochemistry of Dimeric and Mixed-Valence Complexes

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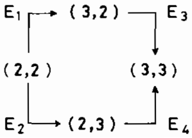
Properties of mixed-valence complexes of transition metals have become the subject of interest [1–5] in the decade or so since the first report of the Creutz–Tabue ion $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$ [6]. The existence of a fixed and generally estimable distance between the two metal centers greatly assists efforts to understand the intramolecular electron-transfer process, or intervalence transfer, in those mixed-valence complexes where it occurs. The effects of metal–metal distance [7], of solution medium [7–9], and of the structure of the non-bridging ligands [10, 11] on the intervalence transfer process have been investigated. Such studies promise to yield important information about inner-sphere and perhaps outer-sphere electron-transfer in general.

If for a given case no side-reactions involving bond breakage or formation occur, the stability of a mixed-valence complex is referenced to the stabilities of its one-electron oxidation and reduction products. Electrochemical measurements on dimeric (or other polymeric [12]) complexes yield the best and most readily available information about such relative stability. For example, if two one-electron voltammetric waves are observed at potentials differing by at least 120 mV at 25 °C, the comproportionation constant, K_{com} (*vide infra*), is greater than 100. This would imply that a mixed-valence molecule is at least $\frac{1}{2}RT\ln(100/4) = 41$ meV more stable than would be expected on the basis of the statistics which alone would predict a K_{com} of 1 to 4. Determination of the magnitude of this stability and of the relationship of observed electrochemical data to the 'one-site energetic electrode potentials' of mixed-valence complexes is the subject of this report.

We might denote a typical transition metal complex dimer with metal oxidation states of a and b in sites A and B, respectively, by (a, b). The one-electron oxidation processes for a typical transition metal dimer (2, 2) are then summarized below.



If there exists no difference in the structure of the dimer at sites A and B, the complex is said to be symmetric. In this case, the two mixed-valence species (2, 3) and (3, 2) are indistinguishable. If instead, sites A and B are of different structure, then in general $E_1 \neq E_2$, $E_3 \neq E_4$, and the mixed-valence species are distinct and of different energy. The quantity $|E_2 - E_1|$ is in fact the difference in energy between the two mixed-valence species (equivalent to E_0 in intervalence-transfer terminology) and is also the best measure of the effect of this structural asymmetry on the dimer's electrochemical properties.

In addition, the oxidation state of site A usually influences the potentials at which site B oxidizes. The quantity $|E_3 - E_2|$ in our example above is a measure of the effect of the interaction between the two metal centers on electrochemical behavior. It is found experimentally that interaction generally *increases* relative stability of the mixed-valence species since the oxidation of site A, for example, usually renders the oxidation of site B more difficult. Such interaction may be of several types: simple coulombic influence (*vide infra*), electronic interaction due to net orbital overlap (generally considered a prerequisite for intervalence transfer to occur), or possibly due to structural deformation on reduction or oxidation.

In equations (1)–(4), the relative concentrations at the electrode of the four relevant species are

$$\frac{[3,2]}{[2,2]} = e^{(E-E_1)/RT} = e_1 \qquad (1)$$

$$\frac{[2,3]}{[2,2]} = e^{(E-E_2)/RT} = e_2 \qquad (2)$$

$$\frac{[3,3]}{[3,2]} = e^{(E-E_3)/RT} = e_3 \qquad (3)$$

$$\frac{[3,3]}{[2,2]} = e_1 \cdot e_3 \qquad (4)$$

calculated using the potential E at the electrode and the three redox potentials E_1, E_2, and E_3. The comproportionation constant, K_{com}, may be defined *om gemera*; for dimeric complexes by equation (5)

$$K_{com} = \frac{([3,2] + [2,3])^2}{[2,2]\,[3,3]} = \frac{(e_1 + e_2)^2}{e_1 e_3} \qquad (5)$$

if (2,3) and (3,2) are considered as distinct species. For the reversible oxidation electrochemistry of the (2,2) complex at a rotating or vibrating electrode in the slow-potential-scan limit for a one-electron oxidation, the calculated current at a given potential E is

$$i(E) = i_d \left\{ \frac{e_1 + e_2 + 2e_1e_3}{1 + e_1 + e_2 + e_1e_3} \right\} \tag{6}$$

Equation (6) is the general equation, derived from Boltzmann distribution considerations, describing the dependence of anodic current on potential E for dimeric complexes given the one-site energetic redox potentials E_1, E_2, and E_3 above. *Calculated voltammograms in quantitative form follow by taking limiting cases of eqn. (6).*

Limiting Case I. A symmetric dimer ($E_2 - E_1 = 0$) is the case proposed for the two terminal metal centers of the trimer $[[(NH_3)_5Ru(pyrazine)]_2\text{-}Ru(bipy)_2]^{8+}$ [8]. For limiting Case I where $E_1 = E_2 = E_3$, eqn. (6) reduces to eqn. (7) and K_{com} will be equal to 4. Note that two

$$i(E) = 2i_d \left\{ \frac{e_1}{1 + e_1} \right\} \tag{7}$$

familiar Nernst-type curves, each corresponding to one one-electron oxidation, are *superimposed.* This lack of potential separation between the two oxidation waves is in contrast to the conclusion [8] that statistics of a dimer satisfying the conditions of Limiting Case I should lead to two oxidation waves separated in potential by RTln(4) = 36 mV. An alternative explanation for the experimentally observed splitting is given below.

Limiting Case II. The majority of mixed-valence dimers studied to date are examples of this case where $E_2 - E_1 = 0$ due to structural symmetry but where there is evidence of significant interaction between the metal centers ($E_3 - E_2 \gtrsim 100$ mV). This interaction causes a separation of the observed oxidation waves. The oxidation polarogram of such (2,2) dimers is closely approximated by eqns. (8) and (9). The first describes a wave centered at a potential of $E_1 - RT\ln(2)$ and the second a similar wave at $E_3 + RT\ln(2)$.

$$\text{for } E \ll E_3,\quad i(E) = i_d \left\{ \frac{2e_1}{1 + 2e_1} \right\} \tag{8}$$

$$\text{for } E \gg E_1,\quad i(E) = i_d \left\{ 1 + \frac{e_3}{2 + e_3} \right\} \tag{9}$$

Thus, for such symmetric complexes there is indeed a statistical contribution to the difference in observed E^0 values of 2RTln(2) = 36 mV at 25 °C. This contribution is, again, *not* present for symmetric complexes with no net metal–metal interaction (Limiting Case I above). This expression for the value of K_{com} in Limiting Case II is given in Eqn. (10).

$$K_{com} = 4\, e^{(E_3 - E_2)/RT} = \frac{4e_2}{e_3} \tag{10}$$

Limiting Case III. Metal complex dimers could conceivably have significantly different structures at site A and site B even while no net interaction exists between them ($E_3 - E_2 = 0$). If the redox behavior is affected significantly ($E_2 - E_1 \gtrsim 100$ mV) by this asymmetry, then the oxidation behavior closely approximated by equations (11) and (12) is expected.

$$\text{for } E \ll E_3,\ i(E) = i_d \left\{ \frac{e_1}{1 + e_1} \right\} \tag{11}$$

$$\text{for } E \gg E_1,\ i(E) = i_d \left\{ 1 + \frac{e_3}{1 + e_3} \right\} \tag{12}$$

This amounts to two one-electron Nernst-type oxidation waves, one centered at E_1 and the other at E_3. The magnitude of the effect of structural asymmetry on electrochemical behavior, $E_2 - E_1$, is reflected directly in the separation in potential of the observed oxidation waves. No statistical contributions exist here. The value of K_{com} is related to the three potentials as in eqn. (13).

$$K_{com} = e^{(E_3 - E_1)/RT} = \frac{e_1}{e_3} = \frac{e_1}{e_2} \tag{13}$$

Limiting Case IV. The final limiting case concerns a dimer possessing *both* significant asymmetry effects ($E_2 - E_1 \gtrsim 100$ mV) and significant net interaction between metal centers ($E_3 - E_2 \gtrsim 100$ mV). The oxidation behavior is approximated in this case by eqns. (11) and (12) above, just as for Limiting Case III, and includes two waves, one centered at E_1 and the other at E_3. In Limiting Cases III and IV where metal site B is significantly more resistant to oxidation than is site A, the (2,3) form is unstable with respect to the (3,2) form and thus is not present to a degree sufficient to cause statistical considerations of the dimer to be different than, say, those of an ion containing only one metal center undergoing 4+ → 5+ → 6+ oxidation.

To summarize the above results, only for symmetric dimers where interaction between the two redox sites is large, that is Limiting Case II, will statistics perturb observed E^0 values derived from true Nernst-type waves away from one-site energetic potentials. It should be noted that there is no discontinuity in the statistical contribution to the separation of observed E^0 values upon slight breaking of symmetry close to the limit $E_2 - E_1 \to 0$. Rather, this contribution is calculated to be $2RT\ln(1 + e_2/e_1)$ from eqn. (5) above for the cases intermediate between Limiting Cases II and IV.

Over the potential range of interest here, the trimer $[[(NH_3)_5)Ru(pyrazine)]_2Ru(bipy)_2]^{6+}$ [8] behaves as though only the terminal two Ru sites are redox active. The voltammogram over this potential was determined [8] to be comprised of two waves separated by about 40 mV. As this separation of waves due to metal–metal interaction is much less than 100 mV, Limiting Case II cannot apply, and the contribution to the observed separation of waves due to statistical effects cannot therefore be as large as 2RTln(2) = 36 mV. The observed separation being due neither to asymmetry nor wholly to statistics must have a contribution from metal–metal interaction. If the distance between terminal metal centers is taken as $\sqrt{2}\cdot 6.9$ Å = 9.8 Å, the coulombic contribution to $E_3 - E_2$ is calculated in acetonitrile (dielectric constant of 37.5) as 39 mV. This electrostatic interaction clearly could account for the observed 40 mV separation between waves.

Limiting cases do not apply for cases where the quantity $E_3 - E_2$ is non-zero but still small (in practice, less than about 100 mV and indicating limited metal–metal interactions). There are actually *no* simplifications of eqn. (6) which will accurately describe the experimental oxidation behavior. In fact, no combination of any finite number of Nernst-type wave shapes which will give the voltammogram expected for the redox behavior of such a dimer. Thus, some method (*e.g.*, non-linear least squares) of refining initial estimates of E_1, E_2, and E_3 in order to simulate most closely an observed voltammogram could yield E_1, E_2, E_3, and thus E_0 of intervalence-transfer for that complex without spectroscopic measurements. Syntheses of dimeric complexes suitable for use in testing this possibility are in progress.

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References

1 G. Tom and H. Taube, *J. Am. Chem. Soc., 97,* 5310 (1975);
H. Krentzein and H. Taube, *J. Am. Chem. Soc., 98,* 6379 (1976);

2 V. S. Srinivasan and F. C. Anson, *J. Electrochem. Soc., 120,* 1359 (1973).

3 D. O. Cowan, P. Shu, F. L Hedberg, M. Rossi and T. J. Kistenmacher, *J. Am. Chem. Soc., 101,* 1304 (1978).

4 F. Felix and A. Ludi, *Inorg. Chem., 17,* 1782 (1978).

5 J.-J. Jwo, P. L. Gaus and A. Haim, *J. Am. Chem. Soc., 101,* 6189 (1979).

6 C. Creutz and H. Taube, *J. Am. Chem. Soc., 91,* 3988 (1969); *95,* 1086 (1973). It is not now clear that this particular complex is in fact mixed-valence; E. Krausz, C. Burton and J. Broomhead, *Inorg. Chem., 20,* 434 (1981).

7 M. J. Powers and T. J. Meyer, *J. Am. Chem. Soc., 102,* 1289 (1980);
M. J. Powers, D. S. Salmon, R. W. Callahan and T. J. Meyer, *J. Am. Chem. Soc., 98,* 6731 (1976).

8 M. J. Powers, R. W. Callahan, D. J. Salmon and T. J. Meyer, *Inorg. Chem., 15,* 894 (1976).

9 M. J. Powers and T. J. Meyer, *Inorg. Chem., 17,* 1785 (1978).

10 S. A. Montague and E. V. Dose, unpublished observations.

11 R. W. Callahan, G. M. Brown and T. J. Meyer, *J. Am. Chem. Soc., 96,* 7829 (1974).

12 A. von Kameke, G. M. Tom and H. Taube, *Inorg. Chem., 17,* 1790 (1978).