Kinetics and Thermodynamics of Coupled Electron-Transfer and Spin-Exchange Reactions

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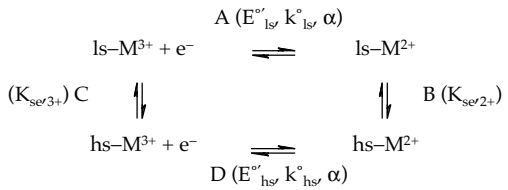
Coupled electron-transfer and spin-exchange reactions occur widely in chemistry and biology (*1*). They constitute an important example of gated electron transfer and may be useful in regulating biological function and controlling molecular device operation (*2,3*).

The present work describes the influence of a coupled spin-exchange reaction on electrochemical behavior in terms of the scheme of squares shown below. Derivations of important quantities are given for this scheme and experimental results are presented for $M(tacn)_2^{3+/2+}$ (M = Ru, Fe, Ni, Co; tacn = 1,4,7-triazacyclononane) and $Fe(pzb)_2^{+/0}$ (pzb^- = poly(pyrazol-1-yl)borate) couples. The position of low- to high-spin equilibrium in the M^{2+} oxidation state is controlled in the former case by changing the metal and in the latter case by changing substituents on the pzb^- ligand.

Spin-exchange contributions to electron-transfer thermodynamics are assessed through measurement of electrochemical half-reactions entropies, $\Delta S°_{rc}$ (*4*). Spin-exchange reactions are entropically driven processes, and molecular contributions to the thermodynamics of spin-exchange and to $\Delta S°_{rc}$ can be quantitatively accounted for in terms of changes in vibrational and electronic partition functions (*5,6*). Kinetic evidence of coupled electron-transfer and spin-exchange is provided by electrochemical activation parameters determined from the temperature dependence of $k_{s,h}$ (*7*). Reactions in which electron transfer precedes a change in spin (low-spin pathway) exhibit values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ that are smaller than reactions that lack this feature. Reactions in which electron transfer follows a change in spin (high-spin pathway) exhibit larger values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. This information is useful in mechanism diagnosis. Results from experimental studies on $M(tacn)_2^{3+/2+}$ (*8*) and $Fe(pzb)_2^{+/0}$ (*9*) systems are presented and compared with derived quantities.



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