The Kinetics of Direct Enzymatic Reduction of Uranium(VI): Effects of Ligand Complexation and U(VI) Speciation

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The kinetics of Fe(III) and U(VI) reduction by AH_2DS is being examined in a systematic manner, through the selection of specific ligands under specific conditions (pH, pCO_2, temp., etc.), to elucidate the effects of complexation on U(VI) bioreduction. Marcus theory is being utilized to develop a fundamental basis and understanding of the electron-transfer reaction in these systems and to develop a predictive structure-reactivity relationship based on first principle calculations and experimental data.

An electron transfer model was developed to determine fundamental rate controls inherent in one-electron, self-exchange reactions in the AH_2DS system and their reduction cross-reactions with Fe(III) complexes. Computed rates for the six one-electron self-exchange reactions in the 9-membered AH_2DS system are all of similar magnitude (10^8 M^{-1} s^{-1}) and in excellent agreement with measured rates (10^6–10^8 M^{-1} s^{-1}). Predicted reduction cross-reaction rates between AH_2DS and the Fe(III)–aquo, –hydroxo, and –organic ligand complexes are in near-quantitative agreement with our measured rates, generally validating an outer-sphere reaction mechanism. The calculations suggest that the observed rate differences are primarily due to differences in the electron transfer distances, the charge of the Fe(III) complexes, and the driving force for electron transfer, while the reorganization energies remain remarkably independent of ligand size. Thus, the main effect of ligand size is a steric one, which directly impacts the electron transfer distance and the "exposure" of the Fe(III) electron-accepting center. Ligand structure directly influences the electron affinity of the Fe(III) center, which in turn also affects the electron transfer rate.

Ongoing experimental studies of U(VI) reduction by AH_2DS have shown that the aqueous uranyl ion and its hydrolysis products are reduced at a significantly slower rate compared with Fe(III). While reduction rates of U(VI)–organic chelate complexes vary with the speciation of uranyl, rates are dependent on solution pH even if the speciation remains the same. While uranyl fluorescence spectra at cryogenic temperatures suggested energy transfer from AH_2DS/AQDS to uranyl ion, which is evidence of encounter complex formation, the reaction mechanism appears far more complicated compared to Fe(III). Work is currently under way to delineate the photophysical effect of uranyl and AH_2DS on the redox kinetics.

Current modeling efforts involve adapting and applying the model for the reduction of U(VI)–aquo, –carbonato, and –hydroxamate complexes. Recent experimental work has shown that UO_2^{2+} reduction rates vary significantly as a function of complexation, but simpler interpretations in terms of ligand structure, reorganization energy, or driving force do not appear to be possible. In addition, the internal reorganization energy may be small, and less dependent on the presence of equatorial ligands in the inner coordination sphere. Therefore, it is anticipated that the current modeling efforts will bring significant insight to bear on the physical quantities that control the reduction rate.