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

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We have been applying density functional theory calculations to estimate the reorganization energy and electronic coupling matrix element Marcus parameters for reduction of the UO_2^{2+} ion. For the reduction of UO_2^{2+} by AH_2DS, the first electron transfer reaction is considered the rate-limiting step, i.e.,

$$AH_2DS^{2-} + UO_2^{2+} \rightarrow AH_2DS^{-\bullet} + UO_2^{+} .$$

Subsequent deprotonation and transfer of an additional electron between the $AH_2DS^{-\bullet}$ radical and U(V) in UO_2^{+} are assumed to proceed extremely rapidly, within the lifetime of the initial encounter complex for the first electron transfer reaction. The reorganization energy is the energy required to manifest a conformation change in the electron donor/acceptor pair and surrounding material that is consistent with the quantum mechanical requirements of electron transfer. Larger reorganization energies usually lead to slower electron transfer rates because more energy must be supplied in order to excite the formation of the transition state. Calculations of the reorganization energy for one-electron transfer reactions involving UO_2-salicylate complexes indicate that the reorganization energy is sensitive to the presence and number of strong chelating ligands in the equatorial plane. For weaker binding ligands, such as H_2O, the effect is smaller but systematic. The intrinsic reorganization energy calculated for reduction of $UO_2^{2+}(OH_2)_x$ where x = 0 – 6 progressively increases from 0.23 eV for x = 0 to 0.61 eV for x = 6. This suggests that increasing ligand numbers should systematically slow down the reduction rate. We are currently evaluating these effects and related quantities for UO_2^{2+} complexed by other ligands with distinctive chelate properties such as carbonate and the siderophore ligands desferrioxamine E and rhototorulic acid.

Experimentally, reduction rates of U(VI) complexes by AH_2DS typically exhibit reaction half-lives ($t_{1/2}$) of more than 20 seconds, and redox behavior of uranyl complexes are clearly dependent on the stoichiometry, the structure of the complex as well as the nature of the ligand. These results are in reasonable accord with Marcus theory calculations. Fluorescence spectroscopic measurements of U(VI), however, are hindered by the severe quenching effect of either AQDS or AH_2DS. Cryogenic time-resolved laser fluorescence spectrometry (CTLFS) at liquid helium temperatures tends to alleviate the quenching problem. Preliminary CTLFS results indicate that spectral measurements are possible but the much broadened U(VI) spectral bands as well as energy transfer effects from AH_2DS to uranyl prevents accurate identification of fluorescent U(VI) species. On the other hand, the observed energy transfer suggests a complex between the uranyl ion and AH_2DS forms, likely as an encounter complex, over the course of the reaction time frame. An understanding of the nature of the formed complex will assist in delineating the reaction mechanism.