Plenary Lectures

Solute–Solvent Interactions in Bioinorganic Chemistry

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The role of solvation in the electron transfer reactions of metalloproteins has been examined. Measurements of the rates of electron transfer reactions between metalloproteins and various inorganic complexes at different temperatures show that the mechanisms employed by hydrophobic and hydrophilic substrates vary significantly. Reactions of blue copper proteins and cytochromes with oxidants such as $Co(dipic)_2^-$ (dipic = dipicolinate) and $Co(phen)_3^{3+}$ (phen = 1,10-phenanthroline) exhibit large positive activation enthalpies and small (in some cases positive) activation entropies. One interpretation of these results is that substantial solvation changes accompany the interaction of the protein with the substrate in the activated complex. Specifically, penetration of hydrophobic substrates into hydrophobic protein interiors is thought to lead to displacement of ordered solvent molecules, thereby increasing entropy. This effect is apparently even larger in electron transfer reactions involving proteins that are believed to be physiological partners.

Solvation of metalloproteins is believed to play a critical role in preventing close approach of reagents with hydrophilic electron transfer surfaces to the protein redox centers. In several cases electron tunneling between redox centers occurs over distances that are determined by the primary solvation shells. These distances have been calculated from electron transfer rate constants determined for several proteins.

Measurements of the redox potentials and the standard enthalpies and entropies for several electron transfer reactions of cytochromes, iron–sulfur proteins, and blue copper proteins have been made. The determination of thermodynamic parameters for protein redox couples was accomplished by measuring the temperature dependence of the electrode potential of suitably designed electrochemical cells. If the electrochemical cell is in a nonisothermal configuration, the experimental temperature dependence, dE°/dT, of the electrode potential can be separated into the following components:

$$dE^\circ/dT = d\phi_{tlj}/dT + d\phi_{tc}/dT + d\phi_f^m/dT$$

ϕ_{tlj} is the Galvani potential difference across the thermal liquid junction within the KCl salt bridge, ϕ_{tc} is the 'thermocouple' potential difference between the hot and cold regions of the working electrode, and ϕ_f^m is the Galvani metal–solution potential difference at the working electrode. Since

$$S^\circ_{red} - S^\circ_{ox} = F\cdot(d\phi_f^m/dT)$$

where F is the Faraday, if $d\phi_{tc}/dT$ and $d\phi_{tlj}/dT$ are constant or can be neglected, partial molal entropy differences for the redox couples of interest can be obtained *directly* from measurements of dE°/dT. It has been proposed that in the nonisothermal electrochemical cell configurations under consideration $d\phi_{tc}/dT < 14\ \mu V/deg$ and $d\phi_{tlj}/dT < 20\mu V/deg$. Since these values are well below the experimental precision of the dE°/dT measurements, we neglect $d\phi_{tc}/dT$ and $d\phi_{tlj}/dT$ in nonisothermal experiments. Furthermore, since $d\phi_{tc}/dT$ and $d\phi_{tlj}/dT$ are constant for a given experimental arrangement, the relative values of dE°/dT for various systems will be unaffected even if these two sources of the observed temperature dependences are not negligible.

We have determined the enthalpy and entropy differences for oxidation state changes in metalloproteins using an optically transparent thin-layer electrode (OTTLE) in a nonisothermal electrochemical cell configuration. The most striking result is that large negative values of ΔS° are obtained for proteins with buried copper or iron sites. Possible interpretations of these ΔS° values include conformational effects as well as solvation changes in the oxidized and reduced states.

Solvent Effects on Molecular Properties

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When molecules collide there may be changes in electronic structure that vary from a minor perturbation to a chemical reaction. The lecture will survey the effects of the environment of a molecule on its structure and properties.