reduction. This apparent anomaly might be explained if N_2, HCN or CH_3NC were either reduced at different sites or bound and reduced by different redox states of the MoFe protein. So, as increasing the ratio of Fe protein-to-MoFe protein increases electron flow, component protein ratio titration experiments in the presence of N_2, HCN and CH_3NC were used. They indicate that HCN and CH_3NC bind to and are reduced at a redox state of the MoFe protein more oxidized than that responsible for either N_2 fixation or H_2 evolution.

Do all substrates and inhibitors of nitrogenase bind to the same site on nitrogenase? Experiments with various combinations of substrates (N_2, HCN, CH_3NC, C_2H_2, N_2O, N_3^-) and inhibitors (H_2, CO, CN^-, CH_3NC) indicate that either C_2H_2 or N_2O stimulate HCN reduction and influence its product distribution, implying simultaneous binding and at least two interaction sites on N_2ase. CH_3NC appears to act as both substrate and inhibitor on binding to the same N_2ase site, implying productive and non-productive modes of binding.

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E8

Thermal and Optical Electron Transfer Probabilities in Biological Systems

N. S. HUSH

Department of Theoretical Chemistry, University of Sydney, N.S.W. 2006, Australia

Electron-transfer reactions are perhaps the most important elementary chemical processes. In ionizing solution, the rates of the simplest of such exchanges (outer-sphere self-exchange between solvated or complex ions) vary enormously — in fact by a factor of $\sim 10^{19}$. The reasons for this very striking behaviour, and also for variation in the rates of cross-reactions, are now thought to be basically understood, as a result of work over the last two decades [1]. It is also known that there is an intimate connection between the probability of thermal exchange and of the corresponding optical or photon-assisted exchange (intervalence transfer) [2]; in principle, the thermal probability can be calculated from the optical transfer probability and *vice versa*. Intramolecular transfer in polynuclear complexes [3] and solid-state transfer (*e.g.* in organic or organometallic semiconductor/metals) can be interpreted within a very similar framework.

Electron transfer processes are very important in biological systems. In these, we are usually faced with the problem that the precise pathway is not known. However, it is known that the overall donor–acceptor distance is often much greater (*e.g.* 15–20 Å) than is usual in simpler systems. There has (mainly as a result of this) been much discussion of the role of tunnelling in biological electron transfer [4], often with the implication that this is of greater importance here than in simpler chemical processes. It is therefore of interest to ask whether one can, at this stage, make useful generalizations about this and other possible determinants of biological transfers. In order to attempt to do so, one must first focus attention on the basic parameters governing transfer probabilities. The most important of these are:

(1) the coupling of electronic to intramolecular vibrational and to phonon modes of the system, and the frequencies involved,

(2) the nature and magnitude of the transfer integral (J) coupling the reactant and product hypersurfaces,

(3) the overall free energy change,

(4) steric factors.

The interplay of factors (1) and (2) will firstly be illustrated by reference to optical transfer in iron–sulphur proteins. The (thermal) frequency factors for transfer rates over large distances will then be discussed with particular attention to the anticipated form of the distance-dependence of J. This is very important, as the electronic transmission coefficient multiplying the frequency factor is (for $J \ll k_BT$) proportional to J^2. It will be shown that there is good reason to suppose that the decrease of J with increasing donor–acceptor distance R in important systems is typically much less than exponential, and may be a fairly low inverse power of R. The magnitude of expected electron–phonon coupling energies and frequencies will also have an important effect in increasing the electronic transmission coefficients. It will be concluded that while nuclear tunnelling plays a significant but minor role at ordinary temperatures, there is at present no need to invoke electron tunnelling as a rate-determining step in typical large-distance biological electron-transfer processes in order to account for their moderate to rapid rates.

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