CHAPTER 14

DYNAMICS OF INTERIONIC ELECTRON TRANSFER

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ABSTRACT. Mechanisms and timescales are described for the transfer of electrons between metal ions (oxidation-reduction). Diffusion of the oxidant and reductant together and the formation of a binuclear intermediate are considered. Criteria are given for the presence or absence of bridging ligands in the latter, and the rate of adiabatic electron transfer is evaluated in terms of a transfer integral and vibrational-electronic coupling. Methods are given for the calculation of the transfer integral from the energies and intensities of metal-to-ligand and ligand-to-metal charge transfer transitions involving the bridging ligand.

1. RATES OF ELECTRON TRANSFER

The most elementary interionic charge transfer reaction between two chemical species A and B is the so-called 'complementary' one, i.e. having 1:1 chemical stoichiometry (1). When a one electron oxidant like Fe$^{3+}$ meets a two-electron reductant like Sn$^{2+}$ the reaction proceeds in steps which are more complicated, and will not be treated here. For the complementary reactions we have

\[
(A^+) + (B) \rightarrow (A) + (B^+) \tag{1}
\]

and the rate of the transfer is \( k[A^+][B] \), where the square brackets denote concentrations. The round brackets in eq.(1) indicate distinct chemical moieties with translational freedom, not just the metal ions between which the electron is being transferred. For instance A and B could be entire cytochrome c proteins with central Fe in the +2 and +3 oxidation states.

In fluid solution the process of eq.(1) is broken down into steps, each with its own rate constant \( k_\text{n} \) as follows:

\[
(A^+) + (B) \xrightarrow{k_1} (A^+\cdot B) \xrightarrow{k_2} (A\cdot B^+) \xrightarrow{k_3} (A) + (B) \tag{2}
\]

Sutin (2) has labelled these four successive states as the initial (1),
precursor (p), successor (s) and final (f). In the precursor, the reactants have diffused together to form a dimeric unit with the correct orientation for the electron transfer, that takes place in step 2, followed by diffusion of the products away from each other. Thus, as in eq.(1) the brackets denote translationally independent entities. Although step 2 is the one of greatest interest to us, the overall rate constant $k$ is determined by all three, and imposing steady state conditions on the intermediate processes we have

$$k = \frac{k_1 k_2 k_3}{k_2 k_3 + k_3 k_{-1} + k_{-1} k_{-2}}$$

or, put in another way

$$1 = \frac{1}{k_i} = \frac{1}{k_1} + \frac{1}{k_{1} k_{2}} + \frac{1}{k_{1} k_{2} k_3} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}$$

where the last three terms represent the rate constants for the processes $i \rightarrow p$, $i \rightarrow s$ and $i \rightarrow f$. Any of these steps could be so much faster than the others that it becomes rate-determining, when of course $k \sim k_1$, $k_2$ or $k_3$.

A particularly important category of electron transfer reactions occurs when A and B are complexes of the same element. This is known as mixed valency (3), and then the p and s states are equivalent. The rate constant $k_2$ is then determined by nuclear rearrangements within the (A.B)$^+$ dimer and by an electronic metal element which will be discussed below.

2. DIFFUSION OF REACTANTS

If the electron transfer step itself is very fast the diffusion of the reactant together ($k_i$) is the rate determining step. Theories of diffusion of ions in solution (Debye equation (4)) allow one to calculate $k_i$ as a function of the charge product $z(A^+)z(B^-)$. The $p \rightarrow i$ dissociation rate constant $k_{-1}$ is obtained from $k_i$ if one knows the equilibrium constant $K_i$ for $i \rightarrow p$. The latter is calculated from the Fuoss equation (5) assuming that the reactants are considered as charged spheres. For example, for complexes with mean ionic diameters of 4Å in a polar solvent, (water) $k_1$, $k_{-1}$ and $K_i$ range from 2.1, 12.2 and -10.0 (in log units) to 11.4, 2.8 and 8.5 for charge products of respectively +12 and -12. Clearly, therefore, the rates $k_{+1}$ are extremely sensitive to the charges of the reactants. Some examples of outer sphere electron transfer rates measured (6,7) for pairs of oxidants and reductants of different charge products are shown in Table 1, compared with the predictions if the reactions were controlled by $k_1(i)$. The orders of magnitude are correct, and the trend is roughly in the observed sense.

When the reaction is diffusion limited the activation energy for