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Topics for Teaching: Proton-coupled Electron Transfer, Part 2

Elephants in the Room, Part 2: Gymnastics for Elementary Particles

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Abstract: The transfer of electrons and protons is compared. Electron transfer over long distances is possible through a series of relays. The range of proton transfer is an order of magnitude less than for electrons but it may be directed along hydrogen bonds.

Keywords: Electron transfer · Hydrogen bonding · Proton coupled electron transfer · Proton transfer

In the first article in this series[1] we looked at the coupling of electron and proton transfer. Here we will compare the dynamics of electron and proton transfer.

Jumping Electrons?

Electrons are often said to jump or hop from one site to another. This is a useful image for humans but elementary particles do not have legs to propel them. We know that the motion of elementary particles must be described using quantum mechanics. Let us look at a very simple electron transfer reaction in which an electron is transferred from a hydrogen atom H_a to a proton H_b^+:

$$H_a + H_b^+ \rightarrow H_a^+ + H_b \qquad (1)$$

Before the reaction, the electron is in the 1s orbital of atom a; after it is in the 1s orbital of atom b. Clearly the two orbitals must interact, and it is usual to take the overlap between orbitals as a measure of the interaction. The equation for the spherical 1s wave function is fortunately very simple: $\psi = 2e^{-\rho r}$ where r is the distance from the nucleus (in Å) and ρ is a constant equal to 1.8 $Å^{-1}$. The exponential term means that ψ decreases rapidly with r, roughly by a factor of 6 for every Ångström, but that it does not actually go to zero. The overlap between two 1s orbitals separated by a distance d also shows this exponential dependence on d.

Chemists have synthesized complexes where two redox centres are separated by a known distance and have studied the rate of electron exchange between the two centres. They find that the rate constant varies with the distance d between the two centres as $e^{-\beta d}$ – as simple overlap considerations would suggest. However, the value of β depends also upon what lies between the donor and acceptor orbitals: it is smaller (*i.e.* the rate is greater) when a network of chemical bonds links the two centres; a typical value is 1 $Å^{-1}$. This question finds practical importance in biological systems where electrons may need to be transported over some distance. Crystal structures of proteins which require long distance electron transfer frequently show electron transfer centres spaced at intervals of 10–15 Å and this distance is often taken as an indication of the separation at which electron transfer may still occur at physiologically sufficient rates. This is analogous to stepping stones across a river (F *pierres de gué*, D *Trittsteine*, I *pietre da guado*) where several short steps allow one to cover a gap which could not be done with one jump. The spaced redox centres not only facilitate the passage, but also, by their position, define the route which is taken. In this they act in the same way as an electric cable in a macroscopic system – but inside a cell.

In Part 1, we saw that a considerable current is involved in the physiological reduction of oxygen and we may now look at this in more detail. The reduction of molecular oxygen is carried out by the enzyme cytochrome c oxidase which spans the membrane of the mitochondrion, an organelle inside the cell.[2] Electrons are delivered from the inside of the mitochondrion and travel through the protein to the active site on the outside of the membrane where dioxygen and protons are delivered. The electron is brought to the enzyme in the form of an iron(II) porphyrin complex inside the protein cytochrome c which binds selectively to a site of the enzyme. After binding, the iron(II) is at a suitable distance from the first redox centre of the protein, a dicopper complex, and the electron is transferred. From there it moves to another iron porphyrin complex inside the enzyme before moving from there to the active site for reduction on the outside of the mitochondrion containing one iron and one copper.

To conclude, electrons may be transferred easily over several Ångströms, and judiciously spaced redox centres allow us not only to extend the range of electron transfer but also to define the route of the electrons.

How far Can a Proton Move?

We now need to look at proton movement. We can start again with a very simple reaction involving a proton transfer between two species:

$$\text{A-H} + \text{B} \rightarrow \text{A}^- + \text{H–B}^+ \qquad (2)$$

For example atom A could be chlorine and B a chloride ion. We stretch the A–H bond and reduce the H–B distance; this is described by vibrational wave functions which we will assume to be those of the simple harmonic oscillator. For the case of HCl, the ground state vibrational wave function contains the exponential term $\exp(-42.6r^2)$ which falls away much faster with distance r than the 1s electronic wave function we saw above. In agreement with the general rules of quantum mechanics, the heavier particle, the proton, is much less delocalised than the electron. We would expect that the interaction between the two vibrational wave functions will fall away much more rapidly with distance and thus that proton transfer will take place over shorter distances than electron transfer. This is indeed the case: proton transfer typically occurs over a range of around 1 Å compared to the distances up to 15 Å observed for electron transfer.[3] If the proton can only move by about 1 Å then AH and B must be close. A–H is a proton donor and B is a proton acceptor so we would expect a hydrogen bond between A–H and B. We may conclude that proton transfer will take place along a hydrogen bond.

This is nicely illustrated in the Grotthus mechanism for proton transport in water:[4] one particular proton is not displaced over long distances, but a series of small proton displacements over hydrogen bonds results in a net transfer of a proton over some distance (Fig. 1).

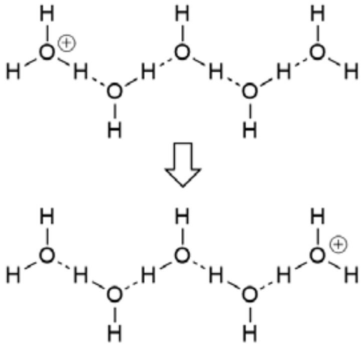
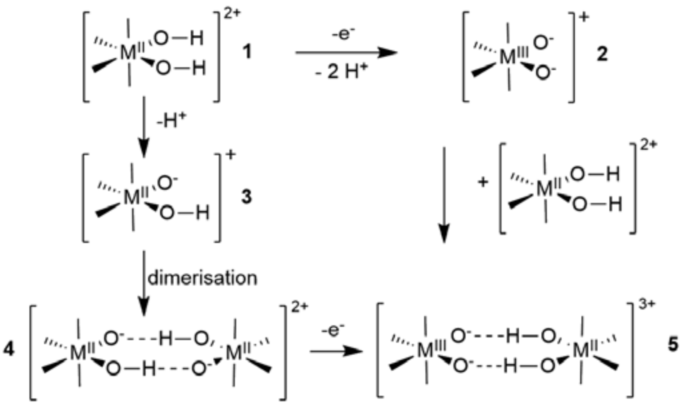


Fig. 1. The Grotthus mechanism: successive displacement of protons along hydrogen bonds moves the positive charge from left to right.



Scheme 1.

This is another example of the long distance transfer over a series of short steps that we saw but over greater distances with electrons.

Concerted Proton-Electron Transfer

An example from coordination chemistry shows how the transfer of protons may be facilitated.[5] The ligand LOH has three coordination sites, an alcohol and two imidazole nitrogens. It forms octahedral complexes $[M(LOH)_2]^{2+}$ with M^{2+} cations (Fig. 2), shown schematically as **1** in Scheme 1. If the metal is oxidised to the +III state, it loses the two alcohol protons to form $[M(LO)_2]^{+}$ **2** as discussed in the first article.[1]

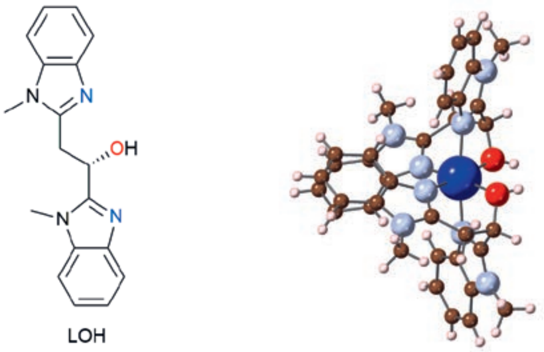


Fig. 2. The ligand LOH (left) can bind through two nitrogens and an oxygen. The octahedral complex [Co(LOH)2]2+ is shown right.

If one titrates **1** with a base, one proton is removed. The mono-deprotonated species **3** has an H-bond donor (the alcohol function) and an H-bond acceptor (the alkoxide). It cannot form an intramolecular H bond, but it can dimerise to form **4** held together by two strong hydrogen bonds – this is why a second proton cannot be removed. A very similar species **5** may be formed by reacting **2** with **1** (the two species need not necessarily contain the same metals), and also has two strong hydrogen bonds.

The M(II) ion in **4** can be oxidised but now the loss of a proton upon oxidation requires only an intramolecular displacement of a proton by about 0.5 Å which is rapid. The cyclic voltammetry of the **5/4** couple is reversible showing electron transfer and proton transfer to be *concerted* and rapid, unlike the **2/1** couple where proton transfer involves the solvent.

Concerted proton-electron transfer is frequently found in biological systems. In photosystem II, which carries out the oxidation of water to molecular oxygen during photosynthesis in plants, algae and cyanobacteria, the photoexcitation of the P680 centre leads to oxidation of a tyrosine residue: the phenolic hydrogen of the tyrosine is hydrogen bonded to an imidazole so that removal of an electron from the tyrosine is accompanied by transfer of the proton to imidazole.[6]

The range of proton transfer may be extended by hydrogen bonded chains as seen for the Grotthus mechanism (Fig. 1) and examples are known where the protons transfer along a chain of alcohol functions or imidazoles.[7] Efficient redox reactions require rapid transfer of both electrons and protons. Compared with electrons, protons are heavy and cumbersome (like elephants) but they should not be overlooked.

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