

Electron Transfer in Chemistry and Biology – The Primary Events in Photosynthesis

V Krishnan

One of the most important chemical reactions is electron transfer from one atomic/molecular unit to another. This reaction, accompanied by proton and hydrogen atom transfers, occurs in a cascade in many biological processes, including photosynthesis. The key chemical steps involved in photosynthesis and the many unsolved mysteries are described in this article.

Introduction

In the centenary year of the discovery of the electron by J J Thomson it would be most appropriate to recount how such a discovery has really enlarged our understanding of many facets of chemistry and biology. Chemistry as it is practised today cannot exist without a proper appreciation of the role of the electron. The concept of a chemical bond as the electron distribution holding atoms together has revolutionised our knowledge about molecules, their structures and stabilities. Our understanding of chemical reactions has also undergone a fundamental change after the discovery of the electron. In gross terms, chemical reactions appear to be addition, removal and rearrangement of atoms. At a deeper level, chemical transformations always involve electrons shifting from one atom or molecule to another thereby creating new molecules.

Consider the well known reactions – oxidation and reduction. They essentially involve oxygen and hydrogen. Oxidation means 'addition of oxygen' and reduction implies 'removal of oxygen'. One can replace this statement by loss or acquisition of hydrogen atoms. With the electrons coming into the scene, oxidation and reduction can be defined as processes which lead to loss and gain



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of electrons, respectively. This has entirely changed the earlier framework of interpreting reactions in chemistry and biology. This shift in emphasis enables one to understand the elementary steps of complex chemical reactions.

In this article, the electron transfer (ET) process is described. Chemical systems in which ET is likely to be facile are first discussed. The important role of ET in many biological processes is then pointed out, with special reference to photosynthesis. Many unusual features in the reaction sequence and current attempts to resolve a few questions are also highlighted.

Electron Transfer in Ground and Excited States

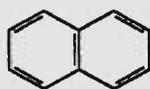
Photo-induced electron transfer (PET) is a very important process, with considerable chemical and biological relevance.

Electrons are not bound equally strongly in all atoms and molecules. Some have greater affinity for the electron than others. Electron rich systems which can readily give up an electron are called Donors (D). Correspondingly, electron deficient units which have the ability to pick up an electron are referred to as Acceptors (A). A few examples of molecules which can function as electron donors and acceptors are shown in *Box 1*.

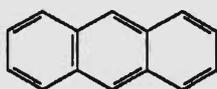
When systems with varying capacity to hold the electron are brought together, there is a likelihood of an electron hopping from the weakly bound to the strongly bound unit. Thus, electron transfer is possible when D and A type molecules are allowed to interact. There is another mode by which electron transfer can take place. By absorption of light of suitable wavelength, molecules (especially those containing chromophoric groups) can be induced to undergo transition from the ground to the excited electronic state. Molecules in the excited electronic state are generally very reactive. They are capable of giving up (or taking in) an electron if efficient acceptor or donor units are available in the neighbourhood. Such photo-induced electron transfer (PET) is a very important process, with considerable chemical and biological relevance.

Box 1. A few Examples of Donor/Acceptor Molecules.

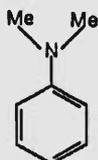
DONOR



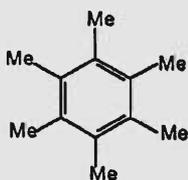
Naphthalene



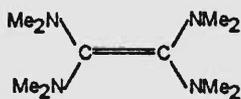
Anthracene



N, N-dimethylaniline

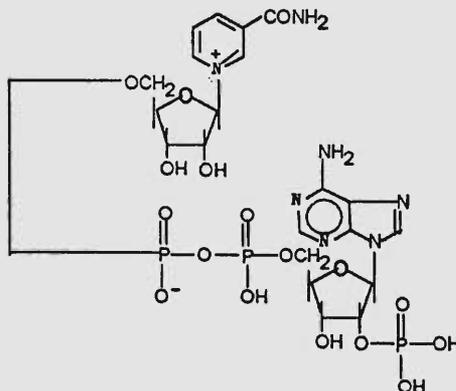
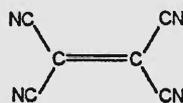


Hexamethylbenzene

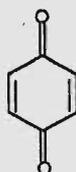


tetrakis(dimethylamino)ethylene

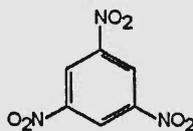
ACCEPTOR

NAD⁺(nicotinamide adenine dinucleotide phosphate, oxidised form)

tetracyanoethylene



p-benzoquinone



trinitrobenzene

Electron transfer reactions can be studied using spectroscopic methods which probe the energetic and spin states of electrons in molecules.

There are many features of the ET process which are of fundamental interest. First, we need quantitative criteria for identifying donors and acceptors. Methods are required to prove the occurrence of electron transfer. The rate of the reaction is, of course, of prime importance. Therefore, techniques which allow measurement of rates of very fast reactions are needed. Finally, a reliable theoretical framework is necessary for interpreting the contributions of various factors which determine the efficiency of electron transfer. In the last few decades, intense research has gone on along these lines.

How well a molecule can function as a donor is related to the ease with which an electron can be taken away from the molecule. Therefore, the ionization energy of the molecule (I_D), which is the minimum energy required to remove an electron from a molecule in its ground state, is an excellent criterion. This quantity can be obtained from photoelectron spectroscopy measurements. In a similar fashion, one can define an acceptor. A good acceptor is one with a higher electron affinity value (E_A), i.e., the energy gained by a molecule on accepting an electron and retaining it within itself. If one knows the I_D and E_A values, one can classify all the molecules in terms of donors and acceptors. Equivalently, donor and acceptor abilities can be quantified in terms of oxidation and reduction potentials.

Armed with the knowledge of donor and acceptor molecules, one can ascertain in a reaction whether the electron really has left the donor molecule or not (alternatively, whether an acceptor molecule has really received the electron from the donor or not). Many different experimental techniques can be used to probe the electron transfer reaction. In certain cases, electron spin resonance would be helpful. It is often easier to monitor the nature of the donor molecule after it has performed its donor function (which means it becomes positively charged) and the negatively charged acceptor subsequent to the receipt of the electron through other spectroscopic methods. New electronic absorption or emission bands may appear. Intensity changes may also provide information about the nature of the species.

The next question is how fast the electron moved from the donor to the acceptor in a reaction. This is an important aspect in chemistry which has large relevance in biological reactions such as certain enzyme functions, photosynthesis and others. The study of fast rate processes has become possible with the advent of lasers. Spectral signatures can be monitored in very short time scales. Reactions occurring in nano (10^{-9}), pico (10^{-12}) and even femto (10^{-15}) seconds can now be studied.

Proteins containing metal ions which can adopt different oxidation states facilitate electron transfer.

The importance of electron transfer lies in the fact that it is often immediately followed by several further reactions. Hydrogen atom and proton transfers are especially facilitated by an initial electron transfer. If the role of the electron is not recognized, the subsequent deep-seated chemical changes would appear to be driven by a mysterious force.

Electron Transfer in Biology

Electron transfer reactions are fast, can occur across relatively well separated units, can be triggered by light and can induce secondary reactions. All these features are fully exploited by nature. Biological processes involve complex reactions dominated by electron and hydrogen movement. There are proteins that facilitate electron transfer from one part to another. A few such systems are listed in *Box 2*.

Box 2. A few examples of Electron Transfer Proteins.

Protein	Metal ions
Cytochromes a, a ₃ , b, c _v , c etc cyt. aa ₃	Fe
Ferrioxins	Fe
Rubredoxins	Fe
Xanthine oxidase	Fe/Mo
Aldehyde Oxidase	Fe/Mo
Succinate dehydrogenase	
Stellacyanin, plastocyanin and azurin	Cu

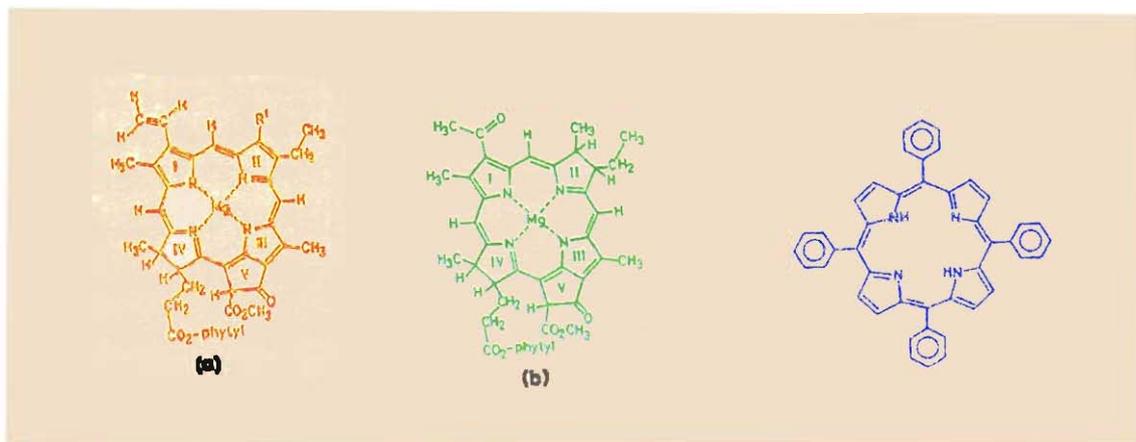


Figure 1. Molecular structure of the plant pigments, tetrapyrrole units. (a) Chlorophyll *a* (Chl), (b) Bacterio Chlorophyll (B.Chl) and (c) a model compound, tetraphenyl porphyrin.

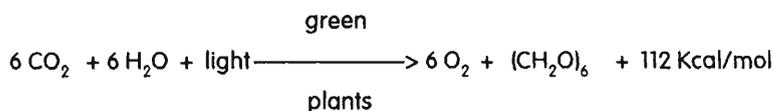
These proteins have metal ions capable of existing in different oxidation states. The ions are embedded in an environment (ligand system) that responds to change in the oxidation states to transfer an electron from one part to another. The important ligand systems are tetrapyrrole macrocycles, *viz.*, porphyrins (Figure 1). Subsequent to the movement of electrons through these arrays of molecules, the electrons are finally captured by biological acceptor molecules. Throughout this electron transfer, there is a corresponding movement of protons elsewhere in the vicinity of the system to maintain the electrical neutrality so as to avoid accumulation of charges.

The electron transfers are manifested in the catalytic conversion processes (enzyme functions) of these substrates. A few such reactions are: (i) conversion of chemically inert molecular nitrogen to the reduced products, (ii) conversion of peroxides to molecular oxygen, and (iii) substitution of oxygen to the organic substrates resulting in hydroxylated and other products. In all these events, electrons are transferred from the enzyme to the substrate with subsequent abstraction of hydrogen from the neighbouring molecules. Prior to the discovery of electrons, it was thought that such reactions occur through some 'reactive intermediates' (catalytic routes) involving hydrogens. The electron transfers between molecules in these systems have qualitatively improved our understanding.

Photosynthesis

Plants have been in existence for a long time even before humans. How do they support themselves and at the same time provide food for other beings? It is through photosynthesis, one of the most fascinating reactions in biology. It is this reaction which sustains life on earth (*Figure 2*). This process provides energy to drive all life's activities such as chemical synthesis, mechanical work, osmotic work, electric signals and others.

In chemical terms, photosynthesis can be represented by a simple equation.



Certain bacterial systems do perform photosynthesis, i.e., synthesise organic matter with the help of light. But instead of H_2O they use other compounds. In terms of oxidation –

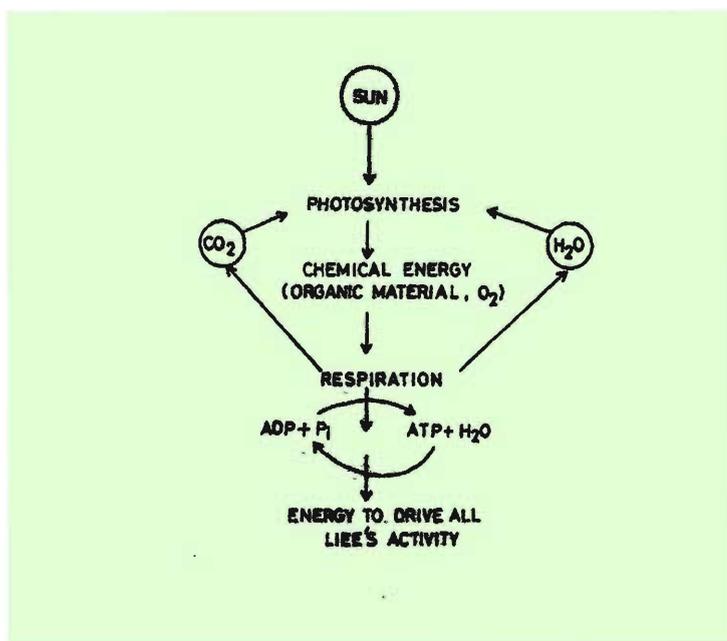


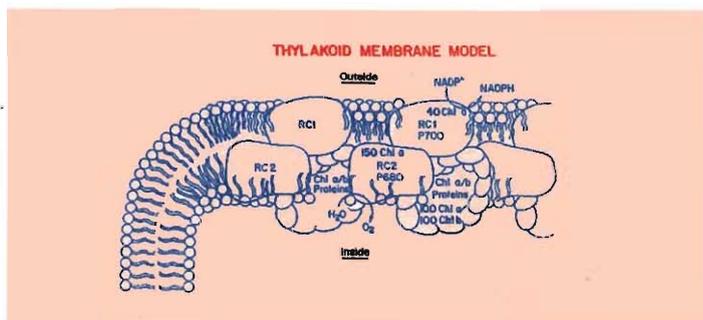
Figure 2. Representation of the various reactions of photosynthesis.

reduction, photosynthesis can be thought of as removal of oxygen from CO_2 and removal of hydrogen from water. Alternately, the reaction involves transfer of hydrogen atoms from water to CO_2 . This was the status of understanding prior to the discovery of electrons. The classification of molecules into donors and acceptors of electrons, the possibility of excited donors and the many experimental methods (laser spectroscopy, photoncounting, 'hole' burning and others) have considerably enhanced our understanding of this complex process.

The photosynthesis process essentially occurs in a membrane composed of two components, light harvesting proteins (LHP) and reaction centre proteins (RC) (*Figure 3*). The primary actions are the harvesting of the light energy from the sun by a large number of chlorophyll molecules and the efficient transduction of energy to an RC complex wherein the electrons are released. The molecular architecture of an RC complex in a membrane bound protein (*Figure 4*) was determined by H Michel, J Deisenhofer and R Huber using X-ray diffraction. This afforded the detailed electron transfer pathways that led to a better understanding of the primary event.

It is found that the light energy is initially received by a 'special pair' bacteriochlorophyll molecule. The primary donor undergoes a rapid charge separation and the electron rapidly cascades through one of the arms to reach an electron acceptor molecule located at the bottom. The charge separation event essentially occurs on photo-irradiation. The sequence of

Figure 3. Thylakoid membrane model showing the possible location of various proteins, light harvesting (LH), reaction centre (RC) and other pigments.



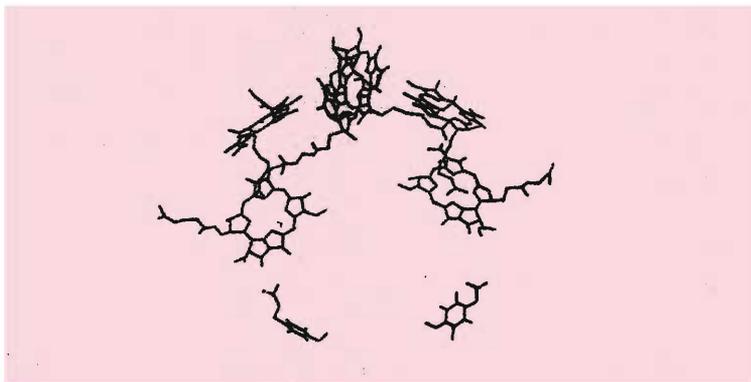
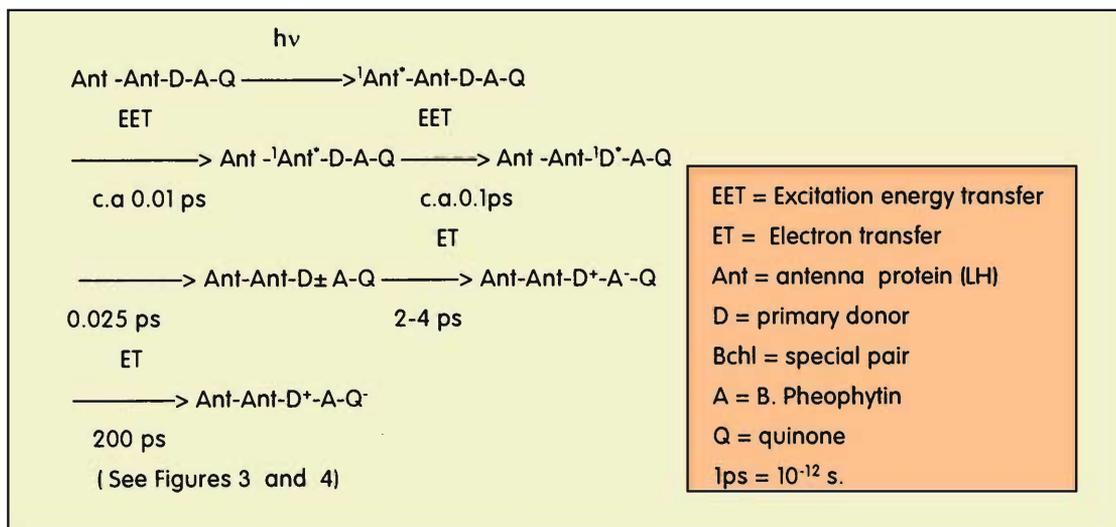


Figure 4. The symmetric arrangement of pigments in the Photosynthetic Reaction Centre of the Bacterium *Rhodospirillum rubrum*. The protein part is not shown. The sequence of pigments are: B. Chl special pair, on the top followed by B. Chl., B. Pheophytin (pigment without the Mg atom) and quinone in the bottom of the figure.

molecules through which the electron from the primary donor passes has been experimentally found and the scheme is given below. The most important aspect of these reactions is that the rate of electron transfer events is independent of temperature in contrast to all the other chemical reactions. Hence primary photosynthetic reactions occur at a relatively low temperature without any change in the efficiency.

There have been a few intriguing aspects in the process that have caught the imagination of chemists. Why does an electron from the primary donor bypass a chlorophyll molecule in the immediate neighbourhood and pass off to a pheophytin molecule and then to the quinones? Why don't the electrons directly reach the quinone? Interestingly, the electron transfer occurs



Suggested Reading

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only through one arm of the entire complex with the molecules on the other arm remaining mute witnesses to the electron passing through. The exceptionally short time scales involved in the ET processes and also their variations are further challenging questions.

In order to derive possible answers, chemists construct and study model molecular systems to duplicate the primary event of photosynthesis. For example, a number of molecules have been synthesized in which donor and acceptor units are placed at prefixed distances and orientations. The rates of electron transfer have been determined. These studies have shown that electron transfer rates between an independent donor and acceptor or covalently linked donor-acceptor combinations depend on many factors such as distal separation between D and A, relative orientation of D with respect to A, the nature of the medium and the nature of the covalent linkage between the D and A.

Among the many model reactions, the simplest one is a donor chemically linked to a series of acceptors and terminating in a quinone. The chemical attachment is essential to put the acceptors in a sequence depending on their electron affinities. The results of these sustained efforts on model reactions have pointed out that there is a requirement of a critical distance of 5 to 8 Å between the donor and acceptor for maximum k_{et} value and proper orientation of D and A molecules so as to have their donor/acceptor orbitals in the right orientation. The solvent medium also plays a very important role in the rate of electron transfers.

The model reactions to mimic primary events have thus far succeeded in matching the rates in electron transfer reactions. However, they have been unable to reproduce the temperature effect. Much more work remains to be done on the natural systems and synthetic models of photosynthesis before we can claim to have understood the role of the electron in this fascinating biological process in its entirety.

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