

Mechanistic Aspects of Redox Reactions of Transition Metal Complexes in Aqueous Media

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Abstract: Transition Metal ions play a very significant and critical role in our biological system, hence the mechanistic study of the reaction of these ions in different chemical environment are of great importance. Inorganic mechanistic study of the transition metal ions suggested their possible way of function in bio system. Also, the study of various modes of chemical reactions guided us to find the possible structural and functional inorganic models of biologically active compounds through which we can easily study and predict the action of bio compounds.

Keywords: Transition metal, outer sphere reaction, inner sphere reaction, PCET

1. Introduction

The chemical process of transferring reactants into products is the subject of studying mechanistic inorganic chemistry. It studies the chemical transformation as a process that occurs in time according to a certain mechanism with regularities characteristic of this process. The development of knowledge on mechanism of transition metal complexes had its beginning in the pioneering research works by S.M. Jorgenson and A. Warner, Lamb and Marden made the first quantitative study in 1911. New advancements in the theory of chemical reactions began with the appearance and development of quantum chemistry. The theory of electron and proton transfer as “simple” models of chemical reactions opened the way for a profound understanding of the quantum-mechanical factors affecting the elementary chemical process and simulated a cascade of experimental studies in chemistry and biology. Chemical kinetics provides variety of methods for investigation of structure and action mechanism of enzyme, one of the greatest creations of nature and this opens the array for chemical modeling of the enzyme reactions. Now, a day’s redox processes of transition metal complexes are probably the best which is understood in chemistry and have seen a strong interplay of theory and experiment.

Mechanism of redox reactions and its classifications

Knowledge of inorganic reaction mechanisms spreads across all areas of the periodic table, covering a wide range of reaction types, geometries and coligands (from classical

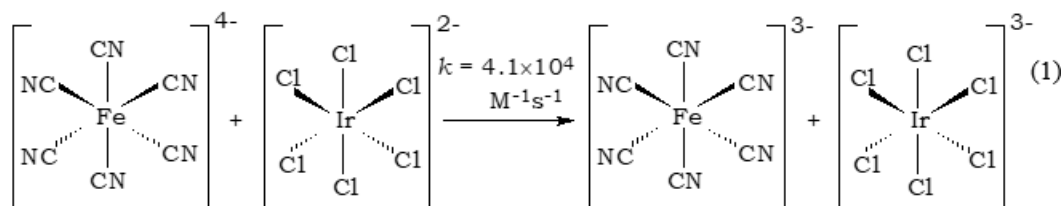
coordination compounds through to organometallics and bioinorganic relevant studies). The principles of mechanistic chemistry present a unifying description of the multitude of reactions that constitutes transition metal chemistry. Electron transfer reactions are a dominant feature of transition metal chemistry, and are of fundamental importance in defining their characteristic. The electron-transfer between two metal complexes may occur by two distinct types of mechanisms: the inner sphere and the outer sphere pathways.

In principle all outer sphere mechanism involves electron transfer from reductant to oxidant with the coordination shells or sphere of each staying intact. Such mechanism is established when rapid electron transfer occurs between two substitution inert complexes and many redox reactions in bio-systems and self exchange reactions occur via the mechanism.

An inner-sphere mechanism is one in which the reductant and oxidant share a ligand in their inner or primary coordination sphere and the electron being transferred across a bridging group *i.e.* a bridged complex between oxidant and reductant is formed before electron transfer occurs.

Outer sphere electron transfer

An outer sphere electron transfer is a reaction in which the electron transfer takes place with no or very weak electronic coupling between the reactants in their transition state. When the reactants are substitutionally robust and do not contain a ligand capable of acting as a bridge to other reactant, the electron transfer is enforced to proceed via the outer-sphere pathway



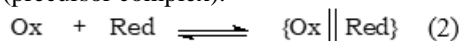
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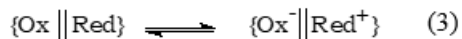
Elementary steps in the outer-sphere mechanism

- 1) A rapid diffusion of the two reagents to form an outer-sphere adduct. (precursor complex).

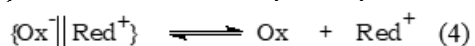


- 2) Chemically activated precursor complex undergoes fast electron transfer, followed by relaxation of the successor complex.

Reactants containing large ligands undergo minimum solvent reorganization, which favours outer-sphere electron transfer rate.



- 3) Successor complex dissociated to the separated products.

**Energy related with the activated Precursor complex**

The free energy associated with the activation of the precursor complex. May be expressed as a sum of three terms:

$$\Delta G^\ddagger = \Delta G_1^\ddagger + \Delta G_2^\ddagger + \Delta G_3^\ddagger \quad (5)$$

ΔG_1^\ddagger = The free energy required to bring the oxidant and reductant into a configuration in which they are separated by a requisite distance (for charged reactants this includes work to overcome the coulombic repulsion).

ΔG_2^\ddagger = The free energy required for bond compression and stretching to achieve orbital of equal energy.

ΔG_3^\ddagger = The free energy needed for solvent reorganisation outside the first coordination sphere.

The Franck-Condon principle states that as a result of the much higher mass of the nuclei, electron transfer occurs much faster than nuclear motion, *i.e.* the nuclear positions are effectively constant in the time taken for the electron to transfer. This is incorporated into the classical electron transfer theories by postulating that the electron transfer occurs at the intersection of two potential energy surfaces, I, one for the reactants (precursor complex) and the other for the products (successor complex). The reactants and the products of equation 6 (self-exchange reaction) have the same energy as shown in figure.1a. At the interaction of potential energy surfaces, (I) electron transfer occur as requirement of equal orbital energies is met. The extent of this interaction is related to ΔE shown in figure 1. When bond distortions are small, coupling interaction is strong and electron transfer is favourable. If the free energy term ΔG_2^\ddagger will be large, *i.e.*, large bond distortion, interaction in potential energy diagram is very weak and the reaction will be slow. These considerations are equally applicable to heteronuclear reactions as described in figure 1b.

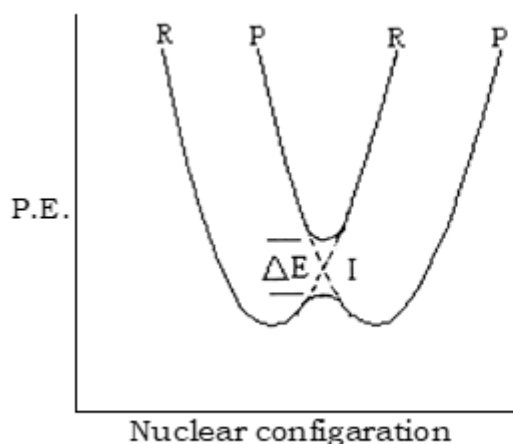


Figure 1a

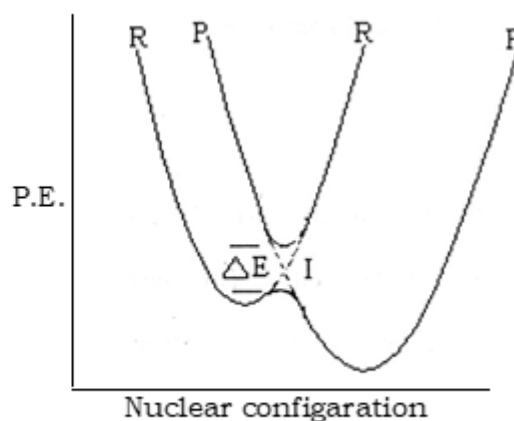
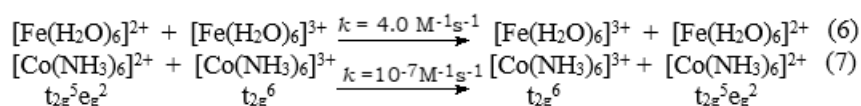


Figure 1b

Figure 1: Potential energy diagram for a homonuclear and heteronuclear reaction

For example, the difference in bond lengths between Fe(II) and Fe(III) is considerably smaller due to presence of same number of electrons in the e_g levels, than the bond length difference between high spin Co(II) and low spin Co(III) as e_g occupation

in Co^{2+} differs by two electrons from Co^{3+} . The activation energy is smaller for the case of Fe system (equation (6)) and the reaction is faster, whereas the similar process is slower for the Co-system (equation 7).

**Cross Reactions and Marcus Relation**

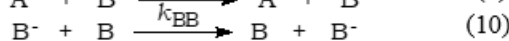
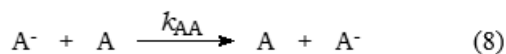
Reactions which proceed by the outer sphere mechanism are well suited to theoretical treatment, developed by Marcus is now referred as Marcus cross relationship or simply Marcus Theory. The electron transfer reaction between a reductant A⁻ and an oxidant B is given by the net reaction where k_{AB} is the

rate constant for asymmetric electron exchange. This cross relationship involves the relationship between the rate constants for the following reactions where equation (8) and equation (9) are called symmetric or self exchange reaction and equation (10) is called cross reaction.

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The theory predicts the rate constant (k_{AB}) for asymmetric electron transfer in an outer-sphere reaction from its equilibrium constant K_{AB} and the symmetric exchange rates (k_{AA} and k_{BB}) for each redox couple A/A^- and B/B^- .

Marcus recognised certain simplifications that lead to the cross relationship (equation 11).

$$K_{AB} = (k_{AA}k_{BB}K_{AB}f_{AB})^{1/2} \quad (11)$$

where, $\log_{10}f_{AB} = (\log_{10}K_{AB})^2 / \{4\log(k_{AA} \times k_{BB}/Z^2)\}$ and Z is the collision number ($\sim 10^{11} \text{ M}^{-1}\text{s}^{-1}$) for the ions in solution. The factor f_{AB} is a correction factor for the difference in free energies of the two reactants and often close to unity. Thus $f_{AB} \sim 1$ unless K_{AB} is large simplifies the equation (11).

$$k_{AB} = (k_{AA}k_{BB}K_{AB})^{1/2} \quad (12)$$

At 25.0 °C for one electron transfer the logarithmic form of the equation (12) becomes

$$\log k_{AB} = 0.5(\log k_{AA} + \log k_{BB}) + 8.46E^\circ \quad (13)$$

Where, E° is the standard EMF of the cross reaction at 25.0 °C.

Table 1: Comparison of some observed rate constants¹¹ ($\text{M}^{-1} \text{s}^{-1}$, 25.0 °C) with those calculated from the Marcus Cross

Reactants	$\log K_{AB}$	$(k_{AB})_{\text{obsd}}$	$(k_{AB})_{\text{calc}}$
$[\text{V}(\text{H}_2\text{O})_6]^{2+} + [\text{Co}(\text{en})_3]^{3+}$	2.12	5.8×10^{-4}	3.1×10^{-3}
$[\text{Ru}(\text{NH}_3)_6]^{2+} + [\text{Co}(\text{phen})_3]^{3+}$	6.25	1.5×10^4	3.5×10^5
$[\text{V}(\text{H}_2\text{O})_6]^{2+} + [\text{Ru}(\text{NH}_3)_6]^{2+}$	5.19	1.3×10^3	2.2×10^3
$[\text{V}(\text{H}_2\text{O})_6]^{2+} + [\text{Fe}(\text{H}_2\text{O})]^{3+}$	16.9	1.8×10^4	1.6×10^6
$[\text{Fe}(\text{H}_2\text{O})]^{2+} + [\text{Ru}(\text{bipy})]^{3+}$	8.81	7.2×10^5	3.6×10^8
$[\text{Ru}(\text{NH}_3)_6]^{2+} + [\text{Fe}(\text{H}_2\text{O})]^{3+}$	11.7	3.4×10^5	1.2×10^7

There was no direct method to measure the self exchange rate of various metalloenzymes. Marcus cross relation can be applied to this bioenzymes but the difficulties usually being attributed to varying points of attack on the enzymes induced conformational changes on enzyme. (1998) Marcus theory is extended to heterogeneous systems also where an extension of the cross-relation for one-phase electron transfer to two-phase case (two immiscible liquids) was made. (1990.1991)

Marcus relation failed in cases of inner-penetration of ligands, change in multiplicity, differences in solution of the hydrophobic/hydrophilic reactants, anharmonicity and a change in the mechanism. Marcus relation is used not only to verify the validity of the proposed outer-sphere paths but also

to predict and calculate reaction rate which are otherwise difficult to measure and also to calculate the concerned redox potential.

Outer-sphere electron transfer may require greater activation than anticipated from Marcus relation, *eg.*, when the redox active site of the redox partners is sterically hindered. (1984) Conspicuous failure of the cross relation are taken as prima-facie evidences of some special effects, *eg.*, non-coulombic interaction, hydrogen bonding and change in mechanism.

Table 2: Some representative examples of outer sphere reactions.

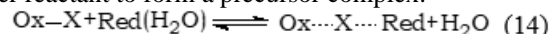
Oxidant	Reductant	Reference
Ethylenebisbiguanidesilver(III) ion	Nitrite	1994
	Oxalic acid	1995
	Glyoxylic acid	2004
	V(II), Cr(II), Eu(II)	1994
$[(\text{cyclen})\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{cyclen})]^{3+}$	2-mercaptoethanol	2004
$[\text{Fe}^{\text{III}}(\text{bpy})_2(\text{CN})_2]^+$	L-Cysteine	2008
$[\text{Ru}^{\text{III}}(\text{edta})(\text{pyz})]^-$	L - ascorbic acid	1996

Inner sphere electron transfer

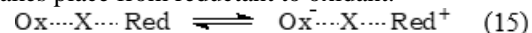
In the inner sphere mechanism, a bridged complex between oxidant and reductant is formed and electron being transferred across the bridging group. The prerequisite condition for inner-sphere mechanism is that one reactant (usually the oxidant) possess at least one ligand capable of binding simultaneously to two metal ions, and the other reactant is substitutionally labile *i.e.*, one ligand must be replaced by the bridging ligand.

Elementary steps for Inner-sphere reaction

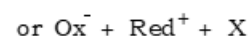
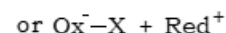
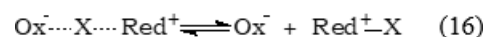
1. Initial diffusion-controlled association of the reductant and oxidant is followed by a substitution reaction in which the bridging ligand penetrates the coordination sphere of the other reactant to form a precursor complex.



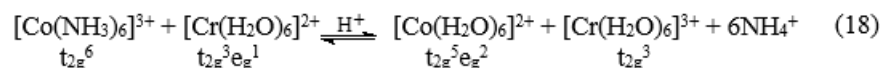
2. At first the precursor complex gets activated and electron transfer takes place from reductant to oxidant.



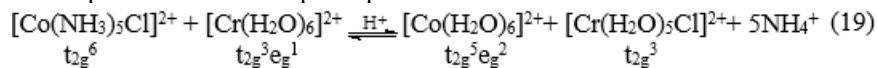
3. Finally the precursor complex dissociates to give products.



This idea of inner sphere mechanism was illustrated by Taube and co-workers. The reduction of hexaamminecobalt (3+) by hexaaquachromium(2+) occurs slowly by an outer sphere reaction and rate of the reaction is $1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$



However, if one ammonia ligand of Cobalt(III) centre is replaced by chloride ion (Cl⁻), then the reaction rate increases ($k = 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), due to presence of a bridging ligand the reaction proceeds via inner sphere path.

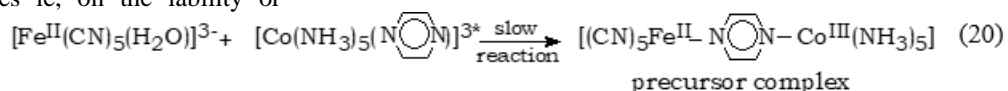


Important factors guiding Inner sphere reaction

1. Taube was first to attempt an explanation of the substitution lability of metal ions by classifying them qualitatively on the basis of their reactivity.
 Labile metal ions: Metal ions react essentially on mixing, i.e., very highly reactive. They have either an empty low energy t_{2g} orbital or at least one electron in high energy e_g orbital.

Inert metal ions: Metal ions react slowly. They have at least one electron in each t_{2g} orbital and no electron in e_g orbitals.

Formation of precursor complex depends upon the rates of substitution in metal complexes ie, on the lability or



3. Role of bridging ligand:

Inner sphere electron transfer reactions are very sensitive to the nature of the bridging ligand, it brings the metal centres together forming an intermediate. Organic or inorganic bridging ligand is the major mediator of the electrons as it travels from one metal to other metal centre. The two possible intimate mechanism of electron transfer within the precursor complex are as follows:

Resonance transfer: In which the electron is transferred directly from one metal to the other by a tunneling mechanism.

Chemical transfer: in which the electron is transferred initially to the bridge and then onto the oxidant.

Various lines of evidences now favour the chemical transfer mechanism in systems containing reducible ligand. The change in the nature of the bridged ligand changes the reaction rate and even reaction mechanism.

inertness of the metal centres. For example, the rates of electron transfer involving $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (d^3) (inert) are comparable to the rate of water substitution.

2. Rate limiting electron transfer:

The electron transfer step will be rate-limiting in systems in which the formation of the precursor complex and decay of the same both are rapid that is when at least one metal center is substitutionally labile, i.e., reaction (19).

Under advantageous conditions, the precursor complex can be detected and the slow electron transfer monitored, which give detailed information about the transfer of electrons within the inner-sphere complex.

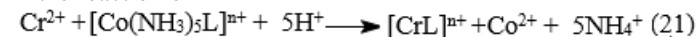
cations. Thus, both $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{py}]^{3+}$ both oxidised Cr^{2+} by an outer sphere mechanism at much slower rate than that when $\text{L} = \text{H}_2\text{O}, \text{I}^-, \text{OH}^-$ and N_3^- .

Table 3: Rate constants (1991) for the reduction $[\text{Co}(\text{NH}_3)_5\text{L}]^{n+}$ by Cr^{2+} , at $T = 25.0 \text{ }^\circ\text{C}$

L	$k, \text{M}^{-1}\text{s}^{-1}$
NH ₃	8.0×10^{-5}
Py	4.1×10^{-3}
H ₂ O	≤ 0.1
I ⁻	3.0×10^6
N ₃ ⁻	3.0×10^{-5}
OH ⁻	1.5×10^6

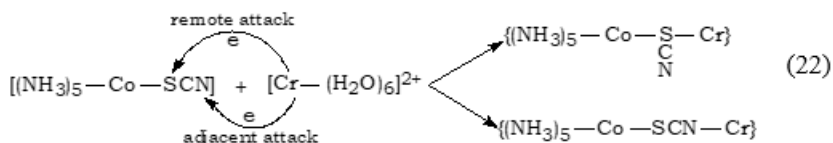
Ligand bridge formation is often rate limiting. When the bridging ligand is ployatomic having more than one potential donor site, there is a possibility for adjacent or remote attack. The selection of mode of attack depends upon the steric, electronic and chemical balance of the attacking centre.

Table 3 shows the alteration of rate on changing bridging ligand in the reaction of

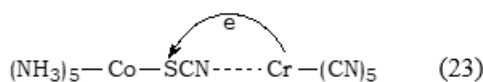


Presence of an unshared electron pair in the co-ordinated ligand L appears a minimum requirement for L to act as a bridging group, for it has to function as a lewis base towards two metal

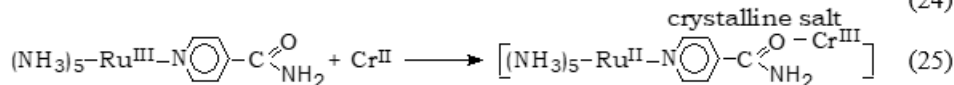
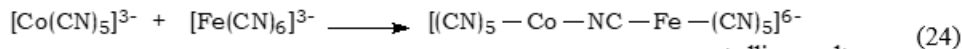
For example, Haim and coworkers found that the reaction of $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{3+}$ with $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ occur by both remote and adjacent attack with almost comparable rate.



But when with soft metal center Co(III) reacts with soft reducing center $[\text{Cr}(\text{CN})_5]^{3-}$ only remote attack on soft 'S' atom takes place.



With the azide (N_3^-) ion as a bridge, a remote attack has generally been assumed.



Spectroscopically the successor complex can be detected in the reaction of $[\text{Ru}(\text{NH}_3)_5(\text{isonicotinamide})]^{3+}$ with $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$.

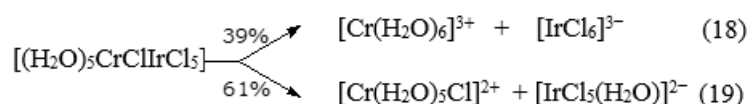
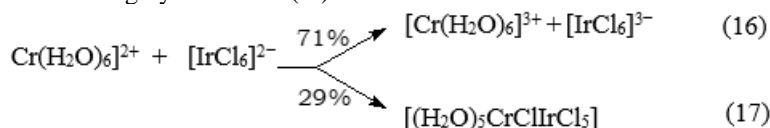
Table 4: Some representative rate constant of inner-sphere reaction.

Oxidant	Reductant	Reference
chromium(VI)	Tyrosine	2008
<i>cis</i> -chloro(dodecylamine)bis(ethylenediamine)cobalt(III)	Iron (II)	2006
<i>N</i> -bromosuccinimide	$[\text{Cr}^{\text{III}}(\text{Dpc})(\text{Asp})(\text{H}_2\text{O})_2]^{2+}$	2004
$[\text{O}=\text{Cr}^{\text{V}}(\text{5-chlorosalen})]^+$	Nitrite	2004
Ethylenebis(biguanide)-silver(III) ion	Benzyl alcohol H ₃ PO ₂ Pyruvic acid	1990 1992 2004
$[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$	N ₂ H ₄ Nitrite	2004 2005

Mixed outer and inner sphere reactions

There are number of reactions where the reaction proceed through both inner and outer sphere mechanism. The reaction of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ with $[\text{IrCl}_6]^{2-}$ operates through both mechanism. At 0° C most of the reaction proceeds via an outer sphere mechanisms and a part of the reaction only forms the

inner-sphere binuclear adduct which then undergoes both Cr-Cl and Ir-Cl cleavage. The outer sphere rate constant for this reaction can be estimated using Marcus equation, as $\approx 10^9 \text{ M}^{-1}\text{s}^{-1}$. This value indicates that outer-sphere pathway is in competition with the inner-sphere path due to presence of a highly labile $\text{Cr}^{2+}(\text{d}^4)$.

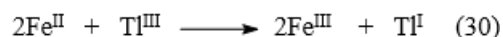


The reduction of horse heart cytochrome C by $[\text{Fe}^{\text{II}}(\text{edta})(\text{H}_2\text{O})]^{2+}$ and $[\text{Fe}(\text{OH})]^{2+}$ by anaerobic acid solution of noradrenaline also proceed via parallel outer and inner sphere mechanism. Oxidation of ascorbic acid both by trioxalatoferrate (III) in weakly acidic aqueous solution and V(V) exhibit parallel inner and outer sphere pathways.

Multiple Electron Transfer

Stoichiometrically redox reactions are of two types,

- 1) Non-complementary Reactions: Reaction in which the change of oxidation states or number of electron of the reacting species are unequal and the stoichiometry is not 1 : 1. for example ,

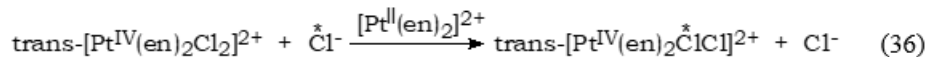


- 2) Complementary Reactions: Reactions in which the formal oxidation states of the oxidant and reductant both change by the same number of units are called complementary reactions.



The energetic requirements to satisfy the Franck-Condon restrictions are too demanding for multi electron transfer. The barrier follows the order: more than two electron \gg two electron $>$ one electron. However, two-electron transfers have been suggested for the oxidation of Hg^{II} by Tl^{III} and for the $Tl^{I/III}$ exchange. The exchange involves a large change of the metal oxygen bond length and the outer shell barrier is four times greater than for a one-electron transfer. These factors

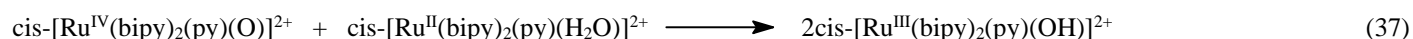
favour one electron transfer mechanism, with Tl^{II} as an intermediate. But the value of equation constant is unfavourable and exchange via Tl^{II} pathways is eight orders of magnitude slower than the measured rate, thus $Tl^{I/III}$ exchange is an authentic example of two electron transfer. One of the best examples of the two electron transfer is the $Pt(II)$ catalysed exchange of free Cl^- for chloride bound to $Pt(IV)$.



Free chloride rapidly attached to the $Pt(II)$ centre forming a five coordinated entity which then forms an inner sphere adduct with $Pt(IV)$ centre. In the adduct the two Pt centres ($Pt(IV)$ and $Pt(II)$) are now in very similar environments and two electron transfer takes place.

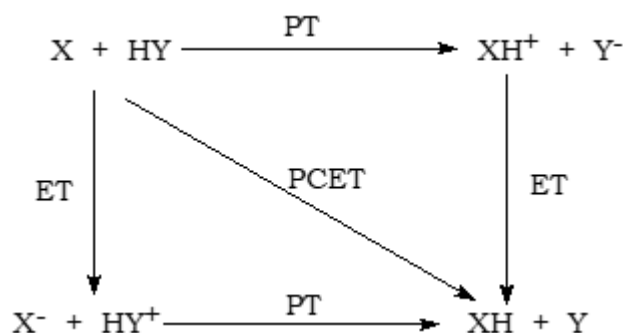
Proton Coupled Electron Transfer

The core of many important energy conversion processes in chemistry and biology are oxidation-reduction reactions in



In this reaction the oxo complex avoids the high energy intermediates $\text{cis-[Ru}^{III}(\text{bipy})_2(\text{py})(\text{O})]^+$ and $\text{cis-[Ru}^{IV}(\text{bipy})_2(\text{py})(\text{OH})]^{3+}$ by undergoing simultaneous e^-/H^+ transfer to give $\text{cis-[Ru}^{III}(\text{bipy})_2(\text{py})(\text{OH})]^{2+}$. According to J. M. Mayer. (2004) PCET refers to a single chemical reaction step involving concerted transfer of both a proton and an electron without any intermediate steps. This definition is explained with the square schemes.

Stepwise reactions where electron transfer (ET) and proton transfer (PT) occur at comparable rates and cannot be separated kinetically, called PCET. The definition of PCET encompasses both hydrogen atom transfer (HAT) and other kinds of concerted electron/proton transfers. Kinetic isotope effects (KIE) are sometime observed for PCET, an example being $k_0(\text{H}_2\text{O})/k_0(\text{D}_2\text{O}) = 16.1$ for the reaction (equation (37)).



Many redox reactions of transitional metal complexes are associated with PCET. Oxidation of H_2O_2 to O_2 by $\text{cis-[Ru}^{IV}(\text{bipy})_2(\text{py})(\text{O})]^{2+}$, (1987) H atom self exchange of $[\text{Fe}^{III}(\text{H}_2\text{bim})(\text{Hbim})]^{2+}/[\text{Fe}^{II}(\text{H}_2\text{bim})_3]^{2+}$ couple (2000) and $[\text{Fe}^{III}(\text{H}_2\text{bip})(\text{Hbip})]^{2+}/[\text{Fe}^{II}(\text{H}_2\text{bip})_3]^{3+}$ couple, redox reactions of different polynuclear manganese complexes, oxidation of hydroquinone and phenols by oxoruthenium complexes

which both electron and protons are transferred. The coupling of electron and proton transfer influences both energetics and mechanism. This coupling is at the heart of water oxidation, respiration, nitrogen fixation and many other key reactions in bioenergetics. In 1981, the term PCET (Proton Coupled Electron Transfer) was coined and applied to the following comprotonation reaction.

belongs to this category. Redox reactions of different polynuclear Mn complexes by glyoxylic and pyruvic acid, nitrite and hydroxylamine described in this dissertation are also associated with PCET in the rate limiting steps.

PCET plays a critical role in the operation of the OEC (oxygen evolving complex) in photosystem II. The movements of protons coupled with electron, avoid excess charge build up, enabling redox potential leveling. PCET also observed in the reduction of oxygen by CytochromeC oxidase,(2003) reduction of hydrogen peroxide by by CytochromeC peroxidase,(1990) deoxygenation rate of oxyHr, (1986) and radical initiation reaction in RNR (2003) and in hydroperoxidation by Lipoxygenase enzyme. (2006)

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