7.5 MARCUS THEORY

Marcus proposed an approximate equation for rate constant of outer sphere electron – transfer reaction. A perusal of fig. 7.2 clearly indicates that the rate of electron transfer depends on two factors; one – the shapes of potential energy diagrams and the other on the standard Gibb's reaction energy. If the parabola in potential diagrams sharply rise, with increase in bond strength, showing increase in energy, then crossing points are high and also the energy of activation. On the other hand, less deep potential curves show low activation energy. Similarly, bigger values of equilibrium inter-nuclear distance show that the equilibrium points are at longer distance. Hence, the crossing point will not be obtained without big distortion. Higher is the value of standard reaction Gibbs energy, lower will be the activation energy of the reaction. Based on all these facts Marcus derived a relation for predicting rate-constant, K, of outer sphere electron-transfer reaction :

$$K_2 = f\, K_1\, K_2\, K$$

where, K_1 and K_2 are rate constants of the two exchange reactions and K is equilibrium constant of the overall reaction.

f, is the function of rate constants and the interaction rate. Generally, its value is taken 1 in all approximate calculations. As the log of rate constants are proportional to activation energy, hence Marcus equation may be expressed in the form of linear free energy relation :

$$2 \text{ In } K = \text{In } k, + \text{In } K$$

$$\text{i.e. } 2\Delta^* G_1 + \Delta^* G_2 + \Delta_t G^o$$

Deviation from Marcus equation is supposed to be a special case in outer – sphere reactions. These cases are due to the obstraction of high to low spin during electron – transfer or due to change in the symmetry. An important example, showing importance of bond distortion magnitude, is self-exchange reaction of hexamine cobalt complexes :

$$[Co^* (NH_3)_6]^{3+} + [Co (NH_3)_6]^{2+} \rightarrow [Co^* (NH_3)_6]^{2+} + [Co (NH_3)_6]^{3+}$$

The rate constant of this slow second order reaction is 10^{-6} M^{-1} S^{-1}.

The characteristics of the reactions are as follows :

(i) Co – N bond Lengths, in Co (II) and Co (III) complexes, are quite different, 2 11 pm and 194 pm respectively,

(ii) Co (II) complexes are high spin complexes (t_2g^5 eg^2) while Co (III) complexes are low spin complexes (t_2g^6 eg^o); and

(iii) after the electron – transfer, the configuration in both the complexes probably becomes t_2g^2 eg^1 and no ion remains in ground state; i.e. they remain in excited state, resulting in increase in activation energy. Because of high activation energy, this reaction is quite slow, as compared to that between $[Fe (CN)_6]^{3-}$ and $[Fe (CN)_6]^{4-}$

Deviation from Marcus theory, otherwise considered as if the reaction is not of outer sphere but is of inner sphere.

Generally, the outer sphere exchange reactions of different metal ions in different oxidation states are faster, as compared to reactions of same ions in corresponding oxidation states. An example of the same is –

$[Os\ (dipy)_3]^{2+} + [Mo\ (CN)_8]^{3-} \rightarrow [Os\ (dipy)_3]^{3+} + [Mo\ (CN)_8]^{4-}$.

The higher rate of these reactions is due to –

(i) In these reactions when the excited state of the product returns to the ground state, the decrease in energy, is obtained in the form of free energy of the reaction (ΔG should be negative, otherwise reaction will not take place).

(ii) It means, the structure of transition state is analogues to the structure of the reactants, hence activation energy remains low and rate increases.

Excited State Outer Sphere Electron. Transfer Reactions

Dramatic change are seen in the redox properties of transition metal complexes, when they are in excited states, absorbing energy. In this field, much work has been done with tris (2-2 bipyridine) Ruthenium (II) Cation ($[Ru\ (bpy)_3)^{2+}$. Specially, because this has possibility of decomposing water by photo-chemical reaction. Thus, this can open the path of the production of hydrogen using solar energy. (Creutz and Sution, 1975).

$$H_2O \xrightarrow[{[Ru^*\ (bpy)_3]^{2+}}]{hv} H_2 + \tfrac{1}{2}\ O_2$$

Here ruthenium complex function as photo-sensitizer. $\Delta G^o = 238$ KJ mol^{-1}

When $[Ru\ (bpy)_3]^{2+}$ absorbs 452 nm light, the very excited state of initial $[^{**}\ Ru\ (bpy)_3]^{2+}$ species changes into quite stable exited species $[Ru\ (bpy)_3]^{2+}$ which in comparison to $[Ru(bpy)_3]^{2+}$, (Ground State Species) is a better oxidant with 2.12 volt (+0.84 V + 1.28 V) and with -2.12 V (-0.86 V + 001.26 V) an outstanding reducing agent (Fig. 7.3)

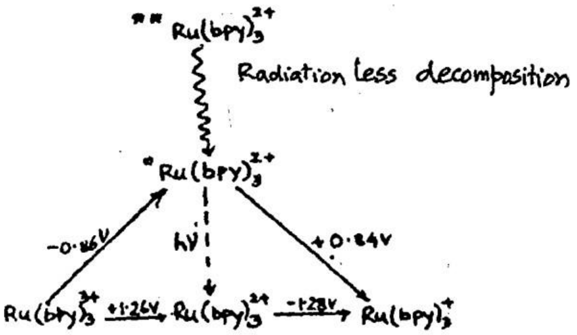

Fig. 7.3

The electronic transfer in the above absorption is a metal to ligand charge transfer, in which one d-electron of ruthenium is exicited and goes to π - antibonding orbital of a bipyridine molecule. Hence in the excited state, the structure of $[Ru^*\ (bpy)_3]^+$ may be written as $[Ru(III)\ (bpy)_2\ (bpy)]^{2+}$. The presence of an electron in an antibonding orbital of a ligand makes this excited state cation quite a better reducing agent, as compared the ground state cation.

Further the hole thus formed in ruthenium, increases its electron accepting capability, resulting in the fact that this excited state. cation, as compared to its ground state, is also a good oxiding agent.