M Sc SEMISTER1

PAPER1

INORGANIC

SUMMARY OF REACTION MECHANISM

SUMMARY

* The reaction in which there is transfer of an electron from one atom to the other occurs and hence the oxidation state of some atoms change, is called 'Redox' reaction.

* These reactions may be divided into two groups :
  (a) The electron exchange process in which no net chemical change takes place. These reactions have outer sphere mechanism and are traced by isotopic labelling and nmr.
  (b) The electron-exchange processes resulting in a net chemical change are called inner sphere or bridge – mechanism redox reactions. These may be traced by common standard chemical or physical methods.

* In outer sphere mecahnism reactions neither the bonds are formed nor broken up, only the oxidation states of metal ions are changed.

* Where both reactants are non-labile eg. in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, a close approach of the metal atom is impossible and the electron transfer must take place by tunnelling or outer sphere mechanism.

* The $[Fe(CN)_6]^{4-}$ - $[Fe(CN)_6]^{3-}$ exchange reaction is catalysed by

alkali metal ions, the effect being greatest for caesium and smallest for lithium.

* Outer, sphere reactions between complexes of different metals (eg. $[Os (dpy)_3]^{2+}$ - $[Mo (CN)_8]^{3-}$ are usually fater than outer sphere exchange reactions between different oxidation states of the same element.

* Electron transfer is expected to be fast when no change in the molecular dimension takes place and the rate constant depends upon the cation present in the solution; ion-pair formation decreases the activation energy by reducing the electrostatic repulsion energy.

* According to the Born-Oppenheir approximation, electron distribution must be done, considering nuclear are stable at their place.

* Accordingly, the possibility of electron transfer will be maximum when the energy of initial and final states are equal.

* For electron transfer it is necessary that the energies of the participating electronic orbitals are equal (Frank – Condon Principle).

* Potential energy diagrams also confirm the relation between molecular motion and electron transfer. For electron transfer it is necessary that there should be coupling in vibrational and electronic motion.

* If the coupling interactions are strong, distortion of bonds is very less and electron transfer is easy.

* According to the non-crossing rule, molecular potential curves of same symmetry-states do not cross each other, but divide into upper and lower curves.

* In common redox reactions, Gibb's energy of the reaction is not zero. If the product surface is high, the crossing point rises and the activation energy will be high.

* Marcus proposed an approximation, giving an equation for rate constant of outer sphere electron – transfer reaction.

Marcus relation is –

$K_2 = f K_1 K_2 K$.

where K_1 and K_2 are rate constants of two exchange reactions and K is equilibrium constant of the overall reaction; while f is the function of rate constants and the interaction rate.

* Redox properties of transition metal complexes in their excited states are quite interesting. Important compound in this regard is $[Ru (bpy)_3]^{2+}$, specially because this has a possibility of decomposing water by a photo-chemical reaction.

* Factors affecting electron transfer reactions are electrostatic repulsion between ions of like charges, the shapes of the molecules, electron reach on the surface of the complex, presence of cation in solution, conductivity of the ligand and the values of ΔG^o.

* Many redox reactions occur by a ligand briding or inner sphere mechanism e.g. $[Co (NH_3)_5Cl]^{2+}$ - $[Cr (H_2O)_6]^{2+}$ reaction. The intermediate formed, dissociates to give a 6 – coordinated Cr (III)

and a 5 – coordinated Co (II) complex.

* No labelled *Cl atoms are found in the chloro-chromium (III) complex when the reaction is carried out in the presence * Cl ions, indicating inner sphere mechanism and no ionisation of the complex.

* Amongst holide ions, the effectiveness for bridging purposes is in the order $F^- < Cl^- < Br^- < I^-$ in accordance with the e^- transmitting tendency.

* The reaction is zero order with respect to one of the components (complexes) and of first order with respect to the other, where bond – dissociation takes place.

* Electron – transfer is rapid only if a conjugate bridged system is formed in the intermediate.

7.9 CHECK YOUR PROGRESS : THE KEY

1. (a) (i) transfer of electron
   - (ii) follow outer sphere
     traced by isotopic labelling and nmr
   - (iii) follow inner sphere
     traced by standard chemical and physical methods.

   (b) (i) are equal
   - (ii) the vibrational stretching and compression
   - (iii) $[Ru(bpy)_3]^{2+}$

2. (a) (i) Six coordinated Cr (III) and 5 – coordinated Co (II)
   - (ii) $F^- < Cl^- < Br^- < I^-$
   - (iii) no lablled *Cl atoms are

indicating that no ionisation

(b) (i) Ligand from one complex

(ii) Zero

and of first order

where bond dissociation

(iii) Conjugate bridge system.