M SC. SEMISTER 1

PAPER 1 INORGANIC REACTION MECHANISM

INNER SPHERE TYPE REACTIONS

Many oxidation-reduction reactions have been shown to occur by a ligand-bridging or inner sphere mechanism in which substitution of the coordination shell of one of the metal ions occurs. The classic example of such a reaction is that between $[Co\ (NH_3)_5\ Cl]^{2+}$ and $[Cr\ (H_2O)_6]^{2+}$ in acidic solution, first investigated by Taube.

$[Co\ (NH_3)_5\ Cl|^{2+}|Cr(H_2O)_6|^{2+} \rightarrow [(NH_3)_5\ Co(III){-}CI{-}Cr(II)\ (H_2O)_5$ .....(7.1)

$[(NH_3)_5\ Co - Cl - Cr\ (H_2O)_5]^{4+} \rightarrow [(NH_3)_5\ Co]^{2+} + [Cr(H_2O)_5\ Cl]^{2+}$ ····· (7.2)

$[(NH)_5\ Co]_2{+} + H_2O \rightarrow [(NH_3)_5\ Co(H_2O)^{2+}$ ························· (7.3)

$[NH_3)_5\,Co(H_2O)^{2+} + 5H_2O \rightarrow [Co(H_2O]^{2+} + 5\,NH_3$ .... (7.4)

The intermediate formed in reaction (7.1) dissociates to give a 6-coordinated (Cr (III) and a 5-coordinated Co (II) Complex [reaction (7.2)] which then picks up the additional water molecule from the medium [reaction (7.3)] to develop into a 6-coordinated Co (II) complex. Being unstable, the Co (II) complex undergoes complete equation to give the hydrated Co (II) ion [reaction (7.4)].

This mechanism is supported by the following facts :

(i) Chlorochromium (III) is formed during the reaction.

(ii) No labeled * Cl atoms are found in the chlorochromium (III) complex when the reaction is carried out in the presence of $*Cl^-$ ions, indicating that no ionization of the complexes takes place.

If the reaction is carried out in the presence of $^{36}Cl^-$ in the solution, none of this isotope appears in the chromium (III) complex; this fact provides further support for the bridging mechanism. Because the change in oxidation states of the metal ions is accompanied by transfer of a chlorine atom, the process is often referred to as an atom transfer reaction.

Similar reactions occur when the chloride in the above example is replaced by other halide ions, sulphate, phosphate, acetate, succinate, oxalate and maleate. Among halide ions, the effectiveness for bridging purposes (as measured by relative reaction rates) is $F^- < Cl^- < Br^- < I^-$, in accordance with the expected order of ability to transmit an electron and undergo covalent bond-breakage. For the organic ions mentioned, oxalate and maleate (which contain conjugated systems) are considerably more effective than acetate and succinate.

There are many other reactions which are believed to proceed by the inner sphere mechanism. Where all the species involved are too labile for tracer methods to be applicable or for the mechanism to be inferred from the nature of the products, dependence of the rate of reaction upon the concentration of an ion present in the solution can provide useful information.

There is some evidence to show that change of anion makes much more difference to the rates of inner sphere reactions (e.g. of $[Cr(NH_3)_5X]^{2+}$ - Cr^{2+} (aq), where X = F, Cl, Br or I) than to the rates of outer sphere reactions (e.g. of the $[Co(en)_3]^{2+}$ $[Co(en)_3]^{3+}$ exchange catalysed by F^-,CI^-or Br^-or I^-). It has therefore been inferred that the F^-, CI^- or Br^- catalysed exchanges between Fe^{2+} and Fe^{3+}, which proceed at about the same rate, are all catalyse outer sphere reactions. This conclusion, however, has been challenged in the case of the chloride ion catalysed reaction, for which it is maintained that detailed interpretation of the kinetics shows that the principal reaction involves atom transfer between $FaCl^{2+}$(aq) and Fe^{2+} (aq).

The consequences of the inner sphere mechanism of the redox reactions are as follows :

(1) Transfer of a ligand from one complex to the other.

(2) The rate cannot be faster than the rate of exchange of the ligand in the absence of the redox reaction.

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

(4) The reaction is first order with respect to the first species if the rate determining step is the attack on the complex.

(5) Electron transfer is rapid only if a conjugated bridged system is formed in the intermediate.

(6) Reactions involving large changes in the molecular sizes are slow.

(7) The rate of reaction between the Cr^{2+} and between CrX^{2+} and between Cr^{2+} and $[Co(NH_3)_5 X]^{2+}$ decreases in the order $I^- > Br^- > Cl > F^-$ showing that the electron transfer through the bridged halogen atom affects the reaction rate.

Check Your Progress – 2

Notes (1) Write your answers in the space given below.

(2) Compare your answers with those given at the end of the unit.

(i) During inner sphere mechanism of redox reaction between $[Co(NH_3)_5Cl]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ the intermediate dissociate to give..................Cr (III) and .... Co (II). Complexes.

(ii) Amongst halide ions, the effectiveness for bridging purposes is in the order ......<...........<.............

(iii) When the reaction is carried out in presence of $^*Cl^-$ ion, ... found in the chlorochromium (III) complex, indicating that .... of the complex takes place.

b (i) Inner sphere mechanism of redox reaction involve transfer of .... to the other.

(ii) The reaction is .... order with respect to one of the complexes and of ....takes place.

(iii) Electron transfer is rapid only if .... system is formed in the intermediate.