



> MainPage

> About College

> Files

> Researches

> Courses

> Favorite Links

> Our Contacts

Visits Of this Page:23



## Research Details :

Research Title : *Tunability of redox potential by ligand conformation a kinetic thermodynamic study*

تنظيم جهد الأكسدة والاختزال بالتحكم في الشكل الفراغي للمتصلة دراسة حركية وديناميكا حرارية

Descriptipn : The effect of ligand conformation on the kinetics and thermodynamics of redox processes were investigated. For this purpose six transition metal complexes viz. hexacyanoferrate(III), tris(oxalate)ferrate(III), tris(1,10-phenanthroline)iron(III), tris(2,2'-bipyridyl)iron(III), hexaisothiocyanatoferrate(III) and tris(acetylacetonato)iron(III) were synthesized and characterized. The free energy change  $\Delta G$  provides a useful indication through which we can compare the relative work potential for different processes, at given set of condition i.e. the thermodynamics of the system, where as the free energy of activation  $\Delta G^\ddagger$  is a measure of the magnitude of the energy barrier to its redox behavior (the kinetics of the system). Since  $\Delta G = -nFE^\circ$ , where  $E^\circ$  is the electrode potential, we obtained the value of  $\Delta G$  from cyclic voltammetry experiments. The  $E^\circ$  values decrease in the order: 2,2'-dipyridyl > 1,10-phenanthroline > acetylacetonato > cyano complex. The remaining two systems are definitely irreversible or are associated (coupled) with side reactions. The kinetic effects were investigated by the study of the reaction of potassium hexacyanoferrate(III) with sodium metabisulfite as a function of pH and at four temperatures, viz. 15, 20, 25 and 30°C. The ionic strength was maintained at 1.0 M, KCl. The pH range used varied between 2.6 to 4.7 using McIlvaine phosphate/citric acid buffer system. The temperature dependences were done for the purpose of obtaining the activation parameters  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . The second order observed rate constant was found to follow an inverse  $H^+$  dependence of the form  $k_{obs} = k_1 + k_2/[H^+]$ . At 298.15 K, the second order rate constant  $k_1 = (1.02 \pm 0.20) \times 10^{-2} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$  and the first order rate constant  $k_2 = (6.33 \pm 0.12) \times 10^{-6} \text{ s}^{-1}$ . The activation parameters for  $k_1$  are:  $\Delta H^\ddagger = 73.64 \text{ KJ mol}^{-1}$ ,  $\Delta S^\ddagger = -36.63 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $\Delta G^\ddagger = 84.56 \text{ KJ mol}^{-1}$  and for  $k_2$  are  $41.71 \text{ KJ mol}^{-1}$ ,  $-205.03 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $102.84 \text{ KJ mol}^{-1}$  respectively. The kinetic data were very well explained by invoking radical mechanism in which the  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  formed  $\text{HSO}_3^*$  and  $\text{SO}_3^{*-}$  radicals, alternatively the redox process could take place by a mechanism in which a fast reversible equilibrium is established between the hydrogen ions and hexacyanoferrate(III), followed by a slow reaction of the protonated species with the sulfite ion leading to the formation of sulfite free radical.

Research Type : Master