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Document Title : *Tunabilty of redox potental by ligand conformation a kinetic thermodynamic study*
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Abstract : 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 ?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 ?G‡ is a measure of the magnitude of the energy barrier to its redox behavior (the kinetics of the system). Since ?G = -n???, where ? is the electrode potential, we obtained the value of ?G from cyclic voltammetry experiments. The E° 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 hexcyanoferrate(III) with sodium metabisulfite as a function of pH and at four temperatures, vis. 15, 20, 25 and 30oC. 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 ?G‡, ?H‡ and ?S‡. The second order observed rate constant was found to follow an inverse H+ dependence of the form kobs?= k1 + k2/[H+]. At 298.15 K, the second order rate constant k1= (1.02 ± 0.20)?10-2 s-1mol-1L and the first order rate constant k2= (6.33 ± 0.12)?10-6 s-1. The activation parameters for k1 are: ?H‡= 73.64 KJ mol-1, ?S‡= -36.63 JK-1 mol-1and ?G‡= 84.56 KJ mol-1 and for k2 are 41.71 KJ mol-1, -205.03 JK-1 mol-1 and 102.84 KJ mol-1 respectively. The kinetic data were very well explained by invoking radical mechanism in which the HSO3- and SO32- formed HSO3* and SO3-* 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.

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