ELECTRON TRANSFER REACTIONS

A thesis presented in candidature for the degree of

Doctor of Philosophy

by

John Ralph McKellar
B.Sc. (Hons.), A.R.A.C.I.
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1.

SUMMARY

The electron transfer reaction between the cobalt (II) and cobalt (III) complexes of acetylacetone has been studied in both acetylacetone and toluene as solvent and it was found that the reaction proceeded much faster in the former. The reaction was found to obey second-order kinetics for the latter solvent and a more complicated kinetics in the former case. The activation energy was calculated and found to be 14.0 and 14.3 kcal/mole in acetylacetone and toluene respectively. The entropy of activation for the system using toluene as a solvent was found to be -40 e.u. while the value for the reaction in acetylacetone can be given an upper limit of - 31.5 e.u. The results from the study of the electron transfer reaction in mixed solvent, viz., acetylacetone with toluene, are interpreted as indicating that the electron transfer, in the presence of acetylacetone in the solvent, occurs by an "outer-sphere" reaction involving a proton bridge.

The study of the electron transfer reaction between the N-phenylsalicylidene-imine type complexes of cobalt (II) and cobalt (III) was carried out in toluene as solvent. The reactions studied were found to obey first-order kinetics, the rate of reaction being dependent on the concentration of the cobalt (III) complexes and independent of the cobalt (II) species. The activation energy of these systems was found to be approximately 13.0 kcal/mole, and this is interpreted as being the energy of activation necessary to
allow the conversion of the diamagnetic cobalt (III) complex to a paramagnetic cobalt (III) complex. Furthermore the activation entropy values were found to be approximately -30 e.u. from which one can deduce that a major contribution to the entropy factor will be the difference in splitting of the energy values of the d orbitals of the reactants.

Pyridine was used as a solvent in the study of the electron transfer reactions between N,N-ethylene-bis(salicylidene-imine) type complexes of cobalt (II) and cobalt (III). These systems gave fast electron transfer reactions which were complete during the time from mixing to separation of the complexes, thus no kinetic data could be calculated for these reactions.

The systems studied have allowed certain deductions to be made as to the effects of a change of ligand and a change of solvent on the rate of reaction and the reactant mechanism. It has been found that a change of the ligand has an effect on the rate of reaction which is most probably due to the change in the ligand field surrounding the complexed metal ion. Further, a change in the solvent for the acetylacetonato complexes has produced a reaction following a complicated kinetics, however this can be explained in terms of solvation of the complexes taking part in the electron transfer reaction, or by the dissociation of "dimer-molecules" formed by the reactants when dissolved in the solvent. It has also been found that the overall charge of the complex molecules does not appear to have any significant effect.
on the rate of reaction. Furthermore, in most of the systems investigated, support was given for the mechanism in which a bridged activated transition state complex is formed, due to the need to transfer a ligand molecule during the electron transfer reaction.