

• CHAPTER - VIII •

CHAPTER VIIISUMMARY

The results obtained from the study of the electrophilic substitution reactions of the metal complexes and the imine complexes are summarised in this thesis. Both the synthetic and the kinetics studies have been investigated. The electrophilic substitution reactions of $n(\text{N-Rsalicylaldiminato})$ metal (n) have been studied kinetically.

The thesis is divided into seven chapters. Chapter I gives a resume of the literature work on the electrophilic substitution reactions of coordinated aromatic ligands. The literature survey on the electrophilic substitution reactions of $n(2,4\text{-pentanedionato})$ metal (n) is also compiled for the comparison. It seems that the aromatic reactive electrophilic site remains unchanged upon coordination although there is a distinct change in the kinetics of the electrophilic substitution reactions of the coordinated ligands as compared to the parent ligands. The literature survey suggests that there is a sufficient scope for the study of the electrophilic substitution reactions of coordinated aromatic ligands. It also seems that the polarisation of an aromatic ring has no spectacular effect on the chemical reactivity of the aromatic

ring except that it has some influence on the rate of the reaction. Literature survey suggested that, it will be promising to carry out a systematic study of the effect of the metal ion on the chemical reactivity of the coordinated aromatic ligand.

Chapter II describes the nature of the present problem. The selection of the ligands is done on the basis of their coordinating capacity with various metal ions. Systematic study of the polarising effect of metal ion on the chemical reactivity of the ligand can be done. The variation of the substituent on the coordinated group will further invoke changes in the electron densities. The complexes $M(\text{sal})_2$; $M(2\text{-hydroxyacetophenone})_2$; $M(2'\text{-hydroxychalcone})_2$ and their imines will be, therefore, ideal for such studies. By using this series of complexes the effect of both the R group and the metal ion on the chemical reactivity of the aromatic ring and on the kinetics of the electrophilic substitutions can be confirmed. In general these complexes are easy to synthesise and are stable under the normal experimental conditions. They are soluble in organic solvents, so that they are easy to handle for the physico-chemical investigations.

Chapter III summarises the results obtained during the nitration reactions of $M(\text{sal})_2$; $M(\text{N-Rsalim})_2$;

M(2-hydroxyacetophenone)₂, M(2'-hydroxychalcone)₂ and their imines, using various nitrating agents. Among the various reagents dinitrogen tetroxide was found to be the suitable nitrating agent with ethyl acetate as the solvent.

1. With complex A, [Ni(Sal)₂] 45 %, 3-nitrosalicylaldehyde; 25 %, 5-nitrosalicylaldehyde and 15 %, 3,5-dinitrosalicylaldehyde was obtained.

2. With complex C, (Cu(Sal)₂) ; 58 %, 3-nitrosalicylaldehyde; 28 %, 3,5-dinitrosalicylaldehyde and 5-nitrosalicylaldehyde was not obtained. Nitration of salicylaldehyde complex using N₂O₄ afforded formation of 3,5-dinitrosalicylaldehyde.

Direct nitration of salicylaldehyde gave 3 and 5-nitrosalicylaldehyde in which major part was 5-nitrosalicylaldehyde. Formation of 3,5-dinitrosalicylaldehyde does not take place. The probable mechanism of the reaction involves an activated complex with metal ion coordinated to dinitrogen tetroxide. Due to such bond formation there is close proximity of the positive end of dinitrogen tetroxide, -NO₂⁺ with the proton at 3 position on the aromatic ring. This steric overcrowding initiates the rupture of the bond between NO₂⁺ - NO₂⁻, yielding 3-nitro derivative. The given mechanism suggests the formation of 3, nitro derivative in higher yield. Cu(sal)₂ gives 3,5-dinitro derivatives, which itself indicates that both steric and electronic factors

associated with coordinated metal ion control the reaction. Same type of nitration reactions were observed in case of 2-hydroxyacetophenone. Nickel complex gave 2,hydroxy-5, nitroacetophenone and 2, hydroxy 3,5 dinitroacetophenone in the ratio of 1.5 : 1 and copper complex gave 1:1.5 respectively. The complex separated from the nitration reaction of copper chalcone complex contained one molecule of coordinated 5', nitro chalcone, one NO_2 and one H_2O group. In addition to the complex, organic ligand 2', hydroxy, 3,5-dinitrochalcone was separated. The nickel chalcone complex gave only the organic ligand. These observations clearly showed that the coordinated metal decided the site of NO_2 substitution and NO_2 enters the coordinated aromatic ring. The nitration reactions of salicylaldimines gave nitrosalicylaldehyde derivatives suggesting that the acid formed during the reaction hydrolysed imine $\text{C} = \text{N}$ bond.

Chapter IV summarises acetoxylation reactions of $\text{M}(\text{sal})_2$; $\text{M}(\text{N-Rsalim})_2$; $\text{M}(\text{chalcone})_2$ and $\text{M}(\text{2-hydroxy-acetophenone})_2$. The reaction of acetyl nitrate with the salicylaldehyde complex gave acetoxyated derivative of salicylaldehyde probably involving the six membered ring formation. Similarly for the first time it was observed that $(\text{CH}_3\text{CO})_2\text{O}$ with salicylaldehyde complexes yielded the 3,acetoxy derivative. This observation suggested that

coordinated metal ion played a definite role in the reaction yielding stereospecific derivative of salicylaldehyde. The metal complex being square planar, approach of acetic anhydride group would be in a plane tilted to the XY plane. Such an approach polarises coordinated salicylaldehyde group and acetic anhydride molecule, 3-acetoxysalicylaldehyde and unstable CH_3CO^- are formed. Acetaldehyde being unstable oxidises to acetic acid. Mechanism of these reactions are suggested.

Acetoxylation reaction of the complex containing M = nickel could not be separated indicating that M-L bond in the nickel complex was labile, compared to copper complex. The acetoxylation reaction of complexes containing 2, hydroxyacetophenone, 2'-hydroxychalcone and N-n-butylsalicylaldehyde could be explained using same mechanism suggested for the acetoxylation reaction of salicylaldehyde metal complexes. It was obvious from the results that the acetoxy group entered in 3 position in an aromatic ring coordinated to metal ion and not in the second aromatic ring present in the complex with 2'-hydroxychalcone. From the acetoxylation reaction of imine 3-acetoxysalicylaldehyde was obtained, which indicated that imine was stable in acetic acid medium. Since nitrous acid is stronger than acetic acid formed in the nitration reactions, the substituted salicylaldehyde formed was hydrolysed.

Chapter V summarises a few chemical reactions of $M(\text{sal})_2$ and $M(\text{N-Rsalim})_2$ such as halogenation thiocyanation and acetoxylation with silver acetate. A few halogenating agents were tried and it was found that halogenosuccinimides were suitable halogenating agents. Reaction of $\text{Ni}(\text{N-n-but-salim})_2$ afforded a mixture of 3,5-dibromo and 5-bromobut-salim. Position of the bromo group was confirmed by ^1H n.m.r. spectra of the ligands, separated from these complexes. For higher ratio of M:NBS the proportion of monobromoderivative was high and for lower ratio, dibromo derivative was high but always a mixture of halogenato complex was obtained. Bromination reaction is slow in parent ligand as compared to the corresponding metal complex. Probaly M-L charge transfer modifies the extent of polarisation in the coordinated ligand, thus reflecting the rate of bromination reaction.

Similarly iodination reactions were carried with $\text{Ni}(\text{N-n-but-salim})_2$ using N-iodosuccinimide as iodinating agent. A mixture of 3,5-diiodo and 5-iodo, N-n-but-salim was obtained. Complexes were characterised by elemental analysis and ^1H n.m.r. spectra of the iodo substituted ligands separated from the above complexes. Ligands were separated by stirring the complex with KCN using methanol as solvent. Pseudo-halogens such as KSCN with salicylaldehyde gave an oily mass

which could not be identified. $\text{Ni}(5, \text{I-sal})_2$ with KSCN gave a novel compound which was characterised as $\text{Ni}(3, \text{SCN}, 5, \text{I-sal})_2$. Structure of this complex was based on elemental analysis, I.R. and ^1H n.m.r. spectra of complex; and the ligand separated from the above complex. $\text{Ni}(5, \text{I-sal})_2$ when treated with silver acetate gave the complex characterised as $\text{Ni}(5\text{-OCOCH}_3, \text{Sal})_2$. Ligand separated was characterised as $5\text{-OCOCH}_3, \text{Sal}$. This indicated that Ag^+ ion present in silver salt catalyses the dissociation of iodo group, and acetoxy group was substituted in place of iodo group.

Chapter VI summarises the kinetics study of the electrophilic substitution reactions of Schiff-base metal complexes. This chapter gives the results of the kinetics study of bromination reactions of bis(N-Rsalicylaldiminato) nickel (II) [R = ethyl, n-propyl, n-butyl, Furyl and iso-butyl] with N-bromosuccinimide in 1,4-dioxane and the two mixtures of 1,4-dioxane and acetonitrile; 95 % + 5 %, 90 % + 10 % respectively. The pseudo first order conditions are carefully monitored during this study. The test tube experiment has shown that the electrophilic substitution reactions of these metal complexes are moderately fast so that the kinetics study of these reactions does not require any sophisticated techniques. These reactions are carried out in dark as they are catalysed by light. Since

the reactions are very slow in an inert atmosphere, they are carried out under the normal atmospheric conditions.

Irrespective of the R group, the plot of absorbance versus time curves for these reactions exhibit two definite stages. The separation of the products during the two stages suggests that the first stage corresponds to the formation of bis(5-bromo, N-Rsalicylaldiminato) nickel (II), and the second stage corresponds to the formation of bis(3,5-dibromo, N-Rsalicylaldiminato) nickel (II). The steep parts during the two stages follow a pseudo-first order rate equation. The activation energy determined for the first stage of the reaction, from the kinetics data at four different temperatures exhibits a direct correlation with the metal-ligand covalency controlled by the R group (except for R = iso-butyl). The trend in the ^1H n.m.r. signals of 7-CH group follows the predicted trend based on the polarisation effect of the R group. Such a polarisation model in the ground state of the complex cannot explain the contradictory value of the activation energy for R = iso-butyl. It seems, therefore, that the polarisation effect of the activated complex will have to be considered to explain the low value of activation energy for the bromination reaction of bis(N-iso-butylsalicylaldiminato) nickel (II). For the second stage of these reactions, the magnitude of the activation energy is not sensitive towards the R group. Thus the polarisation of 3-CH by 5-CBr group seems to be the

dominant factor as compared to the polarisation effect due to the R group.

The effect of the polarity of the solvent on the kinetics study of the bromination reactions of $\text{Ni}(\text{N-Rsalim})_2$ with NBS was also studied. Two different mixtures of 1,4-dioxane and acetonitrile are used. Pure acetonitrile could not be used due to the very fast nature of these reactions in it. However, these reactions could be studied in (i) 1,4-dioxane, 95 % and acetonitrile, 5 % and (ii) 1,4-dioxane, 90 % and acetonitrile, 10 %. The solvent effect on the bromination reaction is observed from (i) The time required to start the reaction is less for the mixture of the solvents than for 1,4-dioxane (ii) The rate of the reaction is faster in the mixture of 1,4-dioxane and acetonitrile as compared to that in 1,4-dioxane, (iii) The rate of the reaction increases with the increase in the proportion of acetonitrile in the mixture of solvents. These observations are substantiated from the lower E_a^I values for the mixtures of the solvents than 1,4-dioxane.

Since the rate of the overall reaction for a given R group depends on the polarity of the solvent, and as the reaction is initiated in an atmosphere containing oxygen (and is catalysed by light) a logical free radical mechanism involving a polar radical intermediate is proposed. Two free

radical mechanisms are suggested for the bromination reaction of allylic compounds (a) Goldfinger mechanism, (b) Bloomfield mechanism. The former involves the formation of hydrobromic acid in one of its steps, while in the latter hydrobromic acid is not formed. The metal complexes studied are acid labile; however during the bromination reaction of these metal complexes there is no indication of their acidic degradation. Thus, the stability of the imine group during the reaction suggests that hydrobromic acid is not formed during the bromination reaction. The Bloomfield mechanism has, therefore, been proposed for the explanation of these reactions. A polar radical instead of a neutral radical will have, however, to be assumed as an intermediate since such an intermediate explains the enormous solvent effect on the rates of the bromination reaction. The polar radical containing the succinimidyl ion discards the objection for the Bloomfield mechanism based on the resonance energy of the succinimidyl radical proposed in the original mechanism. The observation of the definite stages during the reaction suggests that some of the steps are the equilibrium steps in the overall bromination reaction.

The metal ion will have a more pronounced effect on the kinetics of the bromination reaction as compared to the effect of R group. Chapter VII summarises the results of the effect of metal ion [M(n) = cobalt (III), nickel (II), copper (II), zinc (II), palladium (II)] on these reactions.

The free radical mechanism involving a polar radical intermediate explains the activation energy for the first stage of these reactions. Here again Bloomfield mechanism seems to be more logical. The variation of the activation energy for the first stage of the reaction is explained on the basis of the metal-ligand covalency. The thermodynamic parameters of the bromination reaction are compared with ^1H n.m.r. signals and $\nu \text{C} = \text{N}$ group frequencies. The geometry of the metal complex also affects the magnitude of the activation energy. The logical conclusions regarding the kinetics of the bromination reaction on the basis of the metal ligand covalency using the data of the second stage of bromination reaction could not be drawn, as this stage could be studied only for nickel complexes.

Chapter VIII gives the summary of the work reported in the present work.