SUMMARY

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Part- I

Oxidation of N-ligands

Considerable work has been carried out in our laboratories on N-ligands such as oxime-ketones, dioximes, oxime-hydrazones, oxime-semicarbazones, oxime-imines etc. The work mainly involved the studies of these ligands with transition metal ions. The metal chelates formed by these bidentate and related polydentate ligands were studied for their various physical properties. In these investigations, it was observed that the oxime-phenyl hydrazone undergoes oxidation in presence of copper (II) ions, forming oxy-triazole derivative. Search through literature showed that transition metal compounds possess selectivity in oxidising different organic compounds, and that compounds such as mercury (II) oxide and oxides of nitrogen were used in oxidising oxime-hydrazone to oxy-triazole derivative. We further noted that glyoximes were oxidised by oxides of nitrogen, halogens etc. to furoxan derivatives. Hence we planned (1) to prepare vic-oxime-hydrazone and vic-dioxime and (2) to oxidise them with various oxidants to know the selectivity of the oxidants and to propose the oxidant most suited for the oxidation of these ligands. We further attempted to observe the side products of the reaction, if any.

The phenyl hydrazone of 2,3-dioxobutyranilide 2-oxime was prepared and its oxidation was carried out with (1) potassium permanganate under alkaline conditions, (2) manganese dioxide in presence of acetic acid, (3) lead dioxide in presence of acetic acid, (4) potassium ferricyanide under alkaline conditions, (5) iron (III) chloride in presence of hydrochloric acid, (6) copper sulphate and (7) lead tetra-acetate in presence of acetic acid. With these oxidants the oxy-triazole derivative was obtained. (Acid derivative resulting from hydrolysis was obtained with potassium permanganate.) Oxidation could not be effected with per-sulphuric acid and hydrogen peroxide ; and gummy mass was obtained with potassium dichromate.

The relative yield of the product obtained with different oxidants increases in order

$$CuSO_4 < Pb(CH_3CO_2)_4 < PbO_2 \sim MnO_2 < FeCl_3 < K_3[Fe(CN)_6]$$

Hence we suggest that trivalent iron both in the cationic and anionic forms is selective and can be considered suitable for preparative purposes.

We also observe that in presence of hydrochloric acid, the oxime-hydrazone undergoes not only oxidation by iron (III) chloride, but also condensation to the oxime-pyrazolone derivative. Kinetic studies of this reaction were attempted; the results indicate complex nature of the oxidation process.

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2,3-Dioxobutyranilide dioxime was prepared and its oxidation was carried out with (1) potassium permanganate under alkaline conditions, (2) potassium ferricyanide under alkaline conditions, (3) iron (III) chloride in presence of hydrochloric acid, (4) lead dioxide in presence of acetic acid and (5) lead tetra-acetate in presence of acetic acid. In all these reactions, a furoxan derivative was obtained. No reaction could be effected with manganese dioxide in presence of acetic acid and gummy mass was obtained with persulphuric acid, chlorine, sodium hypochlorite, bleaching powder, potassium dichromate etc. With red lead in presence of acetic acid, the dioxime was not oxidised ; however, condensation reaction was observed with the formation of furazan derivative.

The relative yield of the furoxan derivative obtained with different oxidants increases in order

$$K_3[Fe(CN)_6] < PbO_2 < FeCl_3 < KMnO_4 \sim Pb(CH_3CO_2)_4$$

The results show that lead tetra-acetate in presence of acetic acid and potassium permanganate under alkaline conditions may be considered more suitable for the oxidation of the glyoxime to the furoxan.

Part-II

Salts of substituted malonic acids

While studying the preparation and properties of the polymers containing metals, attempts were made in our laboratories to prepare polymers from anionic malonate complexes. These studies necessitated the study of the complexes of substituted malonic acids. The literature survey showed that only a few compounds were known. Hence the study of the salts and complexes of the substituted malonic acids was undertaken. The acids selected were benzylidene malonic acid and its derivatives. The phenyl substituent was selected with a view to understand the steric influences.

The acids were prepared from the substituted benzaldehydes and malonic acid. Their UV absorption spectra were observed. K-band (conjugation band) is observed at 280 mμ in the spectrum of benzylidene malonic acid. The substituent on the phenyl ring causes a shift of the absorption band. The red shift of the band(in alcoholic solution), observed for the para substituent on the phenyl ring increases in order

H < chloro < nitro < methoxy

The variation in shift has been related to the electrostatic and resonance effects.

Introduction of substituents at the ortho,alpha and cis beta positions in the styrene molecule causes

steric interference and twists the essential single bond. The twist angle has been calculated for many styrene derivatives. Benzylidene malonic acid is considered to be a β,β-dicarboxylic acid derivative of styrene. Hence calculations are made for the steric effect of these substituents and the resultant distortion of the molecule from coplanarity. The twist angle was obtained as 30^{o}. The calculations were extended to o-chlorobenzylidene malonic acid, for which the twist angle was obtained as 40^{o}.

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The salts of benzylidene malonic acid and its derivatives with copper, nickel and cobalt were prepared by four different methods : (1) partition method (2) solution method (3) carbonate suspension method and (4) hydroxide suspension method.

The cobalt salts prepared by the first three methods were generally normal salts, while those prepared by the hydroxide method were generally basic salts. The magnetic moments of the normal salts lie in the range of 5.05 to 5.42 B.M. and indicate octahedral stereochemistry of the salts.

The nature of the copper salts prepared by different methods depended much more on the nature of the acid rather than on the method of preparation. And three types of salts-normal,basic and acidic were obtained.

The magnetic moments of the normal salts were found to be about 1.8 B.M. and those of acidic or basic salts were 2.0 to 2.4 B.M.

Nickel salts were obtained by the suspension methods only. Three types of salts- normal, acidic and basic- were obtained. Their magnetic moments varied from 3.4 to 3.6 B.M., irrespective of the nature of the salt.

Zinc and manganese salts were prepared by the partition method only. They are normal salts.

The visible absorption spectra of some copper, nickel and cobalt salts were studied. The bands were suggested to be crystal field bands and attributed to d-d transitions. Using Sugano-Tanabe diagrams and the relations derived by Jorgenson and Ballhausen, various crystal field parameters were evaluated. The crystal field splitting(Δ) was calculated as 8930 cm^{-1} for nickel salt, 9300 cm^{-1} for cobalt salt and 13200 cm^{-1} for copper salt. The results show that the value increases in order

$$Ni^{2+} < Co^{2+} < Cu^{2+}$$

as expected from the spectrochemical series. The values of the crystal field parameters - B, f and h were also evaluated.

The observed magnetic susceptibilities of the copper, nickel and cobalt salts are discussed in terms of the second order Zeeman effect.

The ultra-violet absorption spectra of the salts are compared with those of the corresponding acids and

discussed in terms of conjugation and metal-ligand effects.

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Complex salts of cobalt, nickel and copper with these acids and containing potassium were prepared and their ultra-violet absorption spectra, visible absorption spectra, magnetic susceptibility and electrical conductivity were measured.

From the study of the visible absorption spectra, we find that the crystal field splitting (Δ) is 9300 cm^{-1} for the cobalt complex, 13600-700 cm^{-1} for the copper complexes and 8760 cm^{-1} for the nickel complex. The value increases in order

$$Ni^{2+} < Co^{2+} < Cu^{2+}$$

The order is the same as observed by us for the salts of these metal ions. The value of the crystal field parameter B is also derived.

The molar electrical conductivity of these complexes indicate that the relative dissociation of the complex anion is dependent both on the nature of the metal ion and on the nature and position of the substituent in the acid molecule.

The absorption band in the ultra-violet absorption spectra of these complexes is almost the

same for the complexes of the same acid irrespective of the nature of the metal.

The magnetic moments of these complexes correspond largely to the weak octahedral crystal field with large orbital contribution.