Session Lectures

Photosubstitutions in Transition Metal Complexes

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The number of stereochemical data on d^3-Cr(III) – and d^6-Co(III), Rh(III), Ir(III) – photosubstitutions has been accumulating over the past few years. The experimental data can be rationalized by assuming a dissociative reaction mechanism; one assumes that the primary dissociation is followed (possibly in a more or less concerted way) by an isomerization and an association reaction.

The relevant orbital and state correlation diagrams reveal the reason for the difference in behavior between d^3- and d^6-systems. Both for the axially and the equatorially labilized Cr(III) complexes, it can be shown that the stereomobile reaction is an allowed process, whereas the stereo-retent reaction is a forbidden process.

In d^6-systems, stereomobility as well as stereoretention is observed; the specific reaction path is related to the numerical value of certain ligand field parameters. So far it has been possible to rationalize all the experimental data within the framework of the present methodology.

Mechanism of Octahedral Substitutions on Transition Metal Complexes. Attempts to Distinguish between D and I_d Mechanisms

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A brief survey will be given of research done in our laboratory on mechanisms of substitution in octahedral complexes during the last few years. The mechanism of aquation of the *trans*-chloronitro- and *trans*-dichloro-bisethylenediaminecobalt(III) ions in mixed aqueous solvents favouring the I_d (interchange dissociative) over the D mechanism will be discussed first. Furthermore the mechanism of aquation of (dimethyl sulphoxide) pentaamminecobalt(III) ion will also be discussed in terms of I_d mechanism involving a range of solvents from pure water to water-poor systems [1]. The evidence obtained from studying the induced aquations of $Co(NH_3)_5N_3^{2+}$ and of $Co(NH_3)_5(O_2CNH_2)^{2+}$ [2, 3] by nitrous acid and of $Co(NH_3)_5(halide)^{2+}$ by Hg^{2+} has led to the conclusion, more than 10 years ago, that a common five-coordinated intermediate $Co(NH_3)_5^{3+}$ was formed in all these reactions [4]. Relevant evidence was primarily provided by competition experiments. Recent examinations [5] of different reactions, including $KMnO_4$ induced aquation of $Co(NH_3)_5(DMSO)^{3+}$, suggest [5] different intermediates in different reactions. Our competition experiments [6] on base hydrolysis of $Co(NH_3)_5(DMSO)^{3+}$ will be recalled as showing that the intermediate has some memory of the leaving group. Recently published work on mechanisms of replacement in pentacyano(ligand)ferrate(II) ions in mixed solvents [7–9], and work in progress concerning replacements in the binuclear dimer of $Fe(CN)_5OH_2^{3-}$ will be summarized, and it will be shown that the kinetic results are more consistent with I_d than with D mechanism.

References

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Electron Spin Resonance of Solvent Solute Interactions using Nitroxide Radicals

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It is well known that nitroxide monoradical spectra provide information on their surroundings.