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.

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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.

Hyperfine splitting and Landé factor g variation in isotropic fluid solution can be related to solvent polarity parameters [1–8] (The nitroxide U.V. transition at *ca.* 450 nm may be such a parameter [2]). These properties have been used in spin labelling studies [9–20], although in some cases it is difficult to separate the influence of polarity and motion.

T_2 relaxation time in fluid solution has also been used [7]: various factors influencing this parameter will be discussed.

Pure and mixed solvents have been studied [2, 7] as well as aqueous ionic solutions [21]. Griller has shown the influence of external pressure [22]. Nitroxide biradicals have not received much attention. However, biradicals with large dipolar splitting allow an easy determination of the important parameters [23]. We have described some application to complexation and chiral recognition by cyclodextrins [20, 24, 25]. In solvation studies, these biradicals allow an easy determination of the rotational correlation time τ_c in solution which can be interpreted with a model of solvation [23]. We shall discuss a more accurate determination of τ_c and its application to some solvation equilibrium [26].

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Hydrocarbon Acidities and Brønsted Correlations

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We had previously reported [1] two separate Brønsted correlations relating methanolic sodium methoxide catalyzed hydrogen isotope exchange rates of hydrocarbons with pK_{CsCHA} values. One correlation having a slope of 0.37 at 45 °C applies to fluorenyl and related compounds having a cyclopentadienyl moiety. This correlation has now been extended an additional 2 pK units to higher acidity by study of 1,3-diphenylindene. This compound shows a normal primary isotope effect despite being only 3 pK units less acidic than methanol itself [2]. The second linear correlation having a slope of 0.58 at 45 °C (0.46 at 100 °C) applies to polyarylmethanes. This correlation has been extended up to *p*-methylbiphenyl and toluene without significant deviation. The important region between the two correlations has been studied with derivatives of phenalenes, hydrocarbons as acidic as fluorene and indene but without a cyclopentadienyl moiety. These hydrocarbons actually define the nature of the intersection between two related but different Brønsted correlations.

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