REACTIVITY OF PLANAR TETRACOORDINATE COMPLEXES

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ABSTRACT

Factors affecting the reactivity of complexes involving transition metal ions have been considered and conclusions drawn relating to basicity of a nucleophile micropolarizability, possibility of back-donation via π-bonding, steric hindrance and other aspects.

Square planar four-coordinated complexes of d^8 transition metal ions (such as Pt^{II}, Pd^{II}, Au^{III}, Rh^{I}, etc. are known[1–4] to undergo nucleophilic substitution of a coordinated ligand according to a two term rate law,

$$\text{rate} = (k_1 + k_2[Y])\,(\text{complex})$$

The two rate constants k_1 and k_2 both refer to associative processes, involving the bimolecular attack on the substrate of either the solvent or the incoming nucleophile (Y).

The factors determining the reactivity of a nucleophile Y towards square planar complexes have now been investigated extensively and the following general conclusions have been reached.

(1) The basicity of the nucleophile, expressed in terms of pK_a does not play an important role. In fact, strong bases such as the hydroxide and methoxide ions are practically inactive towards these substrates ($k_2 \ll k_1$). Moreover, Brönsted plots of log k_2 versus pK_a for the entry of amines usually show a small dependence of the reactivity upon the basicity[5–10], except in some very special cases. However, the reactivity of amines, mainly pyridine derivatives, has been extensively investigated, for the purpose of making comparisons between different substrates and in order to obtain a standard measure of the role of steric hindrance in the case of α-methylpyridines. A number of values of the slope α and the steric retardation parameter Δ in the Brönsted plots for different substrates have been collected and used for comparisons[3,4].

(2) The 'micropolarizability' of the entering group, defined as its polarizability in the anisotropic electric field encountered in the transition state, is crucial in determining the reactivity. This factor is usually expressed, as far as platinum(II) complexes are concerned, in terms of n°_{Pt} index[11,12] and the resulting reactivity sequence is, for instance, the following one:

$$Cl^-(3.04) < N_3^-(3.58) < Br^-(3.96) < I^-(5.42) < SCN^-(5.65)$$

The index n°_{Pt}, which is characteristic of each nucleophile, refers to the reaction *trans*-$[\text{Pt(py)}_2\text{Cl}_2] + \text{Y}^- \rightarrow$ *trans*-$[\text{Pt(py)}_2\text{Cl(Y)}] + \text{Cl}^-$ in methanol at 30°C and is defined by the expression

$$n^{\circ}_{\text{Pt}} = \log(k_{\text{Y}}/k_{\text{S}})$$

where k_{Y} is the k_2 value for the nucleophile Y and k_{S} is $k_1/[\text{solvent}]$. The resultant scale can be applied to other platinum(II) complexes according to the expression

$$\log k_2 = S(n^{\circ}_{\text{Pt}}) + \text{constant}$$

The parameter S, usually referred to as the 'nucleophilic discrimination constant', i.e. the slope in the plot of $\log k_2$ versus n°_{Pt}, is characteristic of each platinum(II) substrate and is a relative measure of its ability to discriminate between the various entering nucleophiles. The n°_{Pt} scale can be applied without relevant variations also to palladium(II) complexes, but not to gold(III) derivatives. The explanation for this can be found in a discussion of the role of the central metal in the 'intimate mechanism'; briefly, whereas for platinum(II) and palladium(II) complexes the bond-making and bond-breaking aspects of the substitutions are quite independent from each other, the same is not true for gold(III) derivatives[13].

(3) The possibility of back-donation via π-bonding is also of some importance. Reagents such as NO_2^-, SeCN^- and thiourea ('biphilic') show deviations from the n°_{Pt} scale[14], since they are more reactive than expected when reacting at a negative substrate such as PtCl_4^{2-} and less reactive than expected when reacting with cationic complexes, such as $[\text{Pt(dien)Cl}]^+$. This behaviour has been interpreted in terms of π-bonding effects in stabilizing the transition state.

(4) Other factors can play an important role in determining the reactivity in some special case. Thus steric hindrance must be taken into account when comparing pyridines with α-methylpyridines[5–10]. Anomalies have been observed in the entry of thioethers[15], probably due to some stereo-electronic hindrance since the sulphur donor atom has two lone pairs of electrons. Finally, an interesting observation has been made for the entry of chelating molecules, where during the attack of the first donor site, the presence of the second donor group can assist the substitution of the developing leaving group[16,17].

On facing the problem of reactivity of these compounds, in addition to the factors influencing the nucleophilicity of the entering reagent, one must of course consider also a number of parameters relative to the nature of the substrate, such as the nature of the displaced ligand (X), of the groups which are *trans* and *cis* to it in the ground state, of the nature of the metal and of the solvent in which the displacement is carried out.

As far as the nature of the leaving group X is concerned there is not a constant lability sequence, but the lability seems to be very much dependent on the nature of the reacting system[3,4]. However, in the case of platinum(II) and palladium(II) derivatives the discrimination ability proves to be the same for substrates differing only in the nature of the leaving group. This has been interpreted as a good indication of the asynchronicity of the substitution processes and is a relevant difference between the behaviour of gold(III) compounds and that of the other d^8 metal ion complexes[3,4,18].

The role of the *trans* and *cis* partner(s) on the lability of the displaceable ligand has been studied mainly with platinum(II) complexes. The results obtained indicate that usually the *trans* effect is larger than the *cis* effect[1,2] and this can be related to the different position occupied by the ligands *trans* and *cis* in the trigonal bipyramidal transition state. However, apart from this quantitative difference, the labilizing order for the ligands *trans* and *cis* are qualitatively the same.

In speaking about the *trans* and *cis* effects one must also remember to distinguish between a *trans* (or *cis*) directing influence, as the one originally described in the earlier Russian works on the subject, and the *trans* (or *cis*) labilizing effect, according to the definition proposed by Basolo and Pearson[1], which, referring to kinetics, obviously deals with the difference between the ground and transition states. What is more, the sequence of *trans* labilizing effect has been shown, at least in our case, to be dependent upon the nature of the entering group[19]. If one compares the *cis* and *trans* effects in terms of discrimination the resulting order is qualitatively the same and it corresponds to the order of micropolarizability[11,20].

The nature of the central metal ion is also obviously of fundamental importance in determining the reactivity. There are several data showing that the reactivity increases on moving from platinum(II) to palladium(II) and nickel(II) complexes and also increases on going from platinum(II) to gold(III). There are a few indications which seem to indicate that iridium(I) complexes are less reactive than the platinum(II) complexes.

However, the major difference in the behaviour of compounds of different d^8 transition metal ions was found on discussing the role of the effective nuclear charge in the 'intimate mechanism' of the substitution processes. It has been shown[4,21], for instance, that the synchronicity between the acts of bond formation and bond rupture decreases in the order $\mathrm{Au^{III}} > \mathrm{Pt^{II}} > \mathrm{Pd^{II}} > \mathrm{Rh^{I}}$ and in the case of $\mathrm{Rh^{I}}$ it was possible to detect, kinetically, the formation of a five-coordinated intermediate during the course of the reaction[22].

As far as the effect of the solvent is concerned, it is important in the sense that it can determine in some cases which reaction is taking place[23] but does not affect the order of reactivity and has only a small influence on the discrimination parameters[24,25].

Finally, some studies have been carried out to elucidate the enthalpy and entropy changes which accompany the formation of the transition state. It seems that the rate is mainly controlled by the enthalpy changes and that the entropy of activation is usually largely negative for both the reactions controlled by the k_1 and k_2 rate constants[4,21,26].

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