Coordination Chemistry Reviews, 110 (1991) 213–233
Elsevier Science Publishers B.V., Amsterdam

RECENT DEVELOPMENTS ON THE MECHANISMS OF SUBSTITUTION REACTIONS OF OCTAHEDRAL COORDINATION COMPLEXES

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(Received 12 November 1990; accepted June 1991)

CONTENTS

A. INTRODUCTION

In a recent review, an excellent historical account of the developments in the mechanistic assignments of the spontaneous substitution reactions of Co(III), Cr(III) and, to a lesser extent, Rh(III) complexes was given [1]. However, not all of the conclusions that were drawn with respect to the differences in mechanisms between these metal ions are in accord with the recent results discussed here.

In this article, free energy-mechanistic continuum diagrams will be used to

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[1] Presented, in part, at The XXVII International Conference on Coordination Chemistry, Broadbeach, Queensland, Australia, July 2–7, 1989 (Abstract T89) and The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, U.S.A., December 17–22, 1989 (Abstract INOR 0124).

0010-8545/91/$7.35

illustrate qualitatively the effects of size, π-bonding, solvation and steric interactions on the minimum energy reaction pathways for spontaneous substitution reactions. With the aid of such diagrams, the aquation reactions of $[M(NH_2R)_5Cl]^{2+}$ (R = H, CH_3; M = Co(III), Cr(III), Rh(III)) are discussed in detail, and a critical analysis is made with regard to some of the assertions made in the review by Mønsted and Mønsted [1] on our early work in this area [2–6]. A more extensive review of recent developments in the mechanisms of spontaneous and base-catalysed substitution reactions has been published elsewhere [2].

(i) The mechanistic continuum and mechanistic nomenclature

A commonly overlooked aspect of substitution reactions is that there exists a continuum of mechanisms for a particular type of reaction, rather than two or more discrete mechanisms. Thus, for spontaneous substitution reactions, organic chemists refer to S_N1 and S_N2 mechanisms, whereas inorganic chemists often refer to D, I_d, I_a and A mechanisms. The use of such labels tends to give a false impression of a discrete mechanism for each label. This, in turn, leads to a difficulty in appreciating that any perturbation of a chemical system (changes in steric interactions, solvation, π-bonding, etc.) will affect the position of the preferred mechanistic pathway (lowest activation energy) on a mechanistic continuum. This can occur without necessarily altering the mechanistic label itself within the ambit of the traditional labels that have been used.

A further difficulty arises due to the different working definitions of I_a and I_d that have been adopted by various researchers. The working definition that was originally adopted by Langford and Gray [7] for an I_a mechanism, is that there is synchronous bond making with the incoming group and bond breaking with the leaving group, such that the incoming nucleophile is involved in the activation of the metal-leaving-group bond. If a transient intermediate of increased coordination number is formed in the activation process, it is shorter-lived than the time scale of solvent reorganization and hence, effectively, there is only a transition state. Conversely, for an I_d mechanism, the "activation energy is determined by the requirements of dissociation". Therefore, the leaving group is effectively lost from the first coordination sphere in the activation process. The intermediate of reduced coordination number has a shorter lifetime than that required for solvent reorganization which differentiates an I_d mechanism from a D mechanism. In theory, the definitions of Langford and Gray allow the separation of mechanisms in terms of the sensitivities of the rate constants of the reactions to the natures of the incoming nucleophiles. However, this rationale for assigning a mechanism cannot be applied to solvent self-exchange reactions, since the entering group and the leaving group are the same, by definition. An alternative definition of I_a and I_d was suggested by Merbach [8,9] in order to overcome these difficulties. In Merbach's nomenclature, a mechanism that involves more bond breaking than bond making in the transition state is defined as an I_d mechanism, and has a positive volume of activation. In contrast, a mechanism that involves more bond making than breaking in the transition state is defined as an I_a mechanism, and has a negative volume of activation.

Apart from the problems that arise from using a two-compartment classification of a continuum of interchange mechanisms, the different nomenclature that has arisen has led to further misunderstandings and conflict in the literature. This is apparent where different researchers have used different working definitions to describe the mechanisms of the same reactions. Although Mønsted and Mønsted have recognized some of the problems in the use of I_a and I_d nomenclature, no recognition of the different working definitions used by different workers is evident in Table 1 and associated text in their review [1]. An excellent account of the problems and confusion that have arisen from the use of different mechanistic definitions for the same labels is given in the reviews by Swaddle [10] and Tobe [11]. Due to these problems in classification, some authors prefer to not use labels at all, but rather use descriptions such as, bond breaking substantially precedes bond making, or bond making substantially precedes bond breaking [12]. Alternatively, relative terminology is used in order to compare similar complexes, e.g. more/less, associative/dissociative [1].

(ii) Classification of mechanisms

Most spontaneous substitution reactions of octahedral complexes occur via mechanisms in which there is no discrete intermediate of lifetime longer than solvent reorganization, i.e. they are interchange mechanisms. Throughout this discussion, the terminology of Merbach will be used to describe interchange mechanisms. Figure 1 (adapted from refs. 2, 8 and 9), illustrates some of the different transition states and intermediates that are possible for a spontaneous substitution reaction. As pointed out by Merbach [8,9], between the discrete boundaries which are formed by an associative mechanism (A) or a dissociative mechanism (D) lies a continuum of interchange mechanisms. These mechanisms are classified further as associative interchange (I_a), in which bond making precedes bond breaking, interchange (I), in which there is an equal amount of bond making and breaking in the transition state, and dissociative interchange (I_d), in which bond breaking precedes bond making. The qualitative relationships between the nomenclatures of Langford and Gray, and of Merbach are given in Fig. 1. Thus, a mechanism that is correctly assigned as I_a using the definition of Langford and Gray may also be correctly assigned as I_d using the definition of Merbach. This is because an incoming nucleophile may still have an influence on the activation process even though there is more bond breaking than making in the transition state. This highlights the need for authors to state which of the working definitions they use in papers that contain the I_a/I_d nomenclature.

Whilst the use of such labels is convenient, it does not reflect the continuum nature of substitution reactions shown in Fig. 1. Moreover, two reactions may be correctly assigned to have the same mechanistic label (e.g. I_d), but within the context

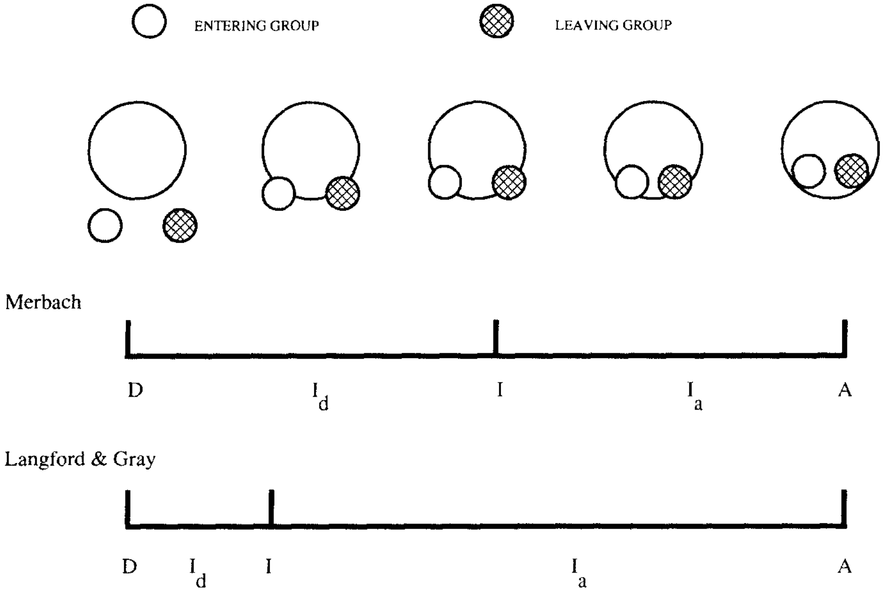


Fig. 1. Classification of the mechanisms of spontaneous substitution reactions, according to Langford and Gray [7] and Merbach [8,9]. (The separation of the two classifications is made at an arbitrary point on the mechanistic continuum for the Langford and Gray nomenclature. This diagram is only used to illustrate qualitatively the differences in the two mechanistic nomenclatures.)

of the mechanistic continuum, they could have very different mechanisms (i.e. one mechanism could be close to the dissociative limit and the other could be close to the pure I mechanism). Conversely, two mechanisms that are closer together in the mechanistic continuum may have different mechanistic labels if they are towards the middle of the continuum. Such problems have been recognized by a number of authors [1,2,8–11,13,14], but often they are not addressed adequately in research papers.

In order to overcome some of the confusion, it is proposed that qualitative free energy diagrams containing a mechanistic coordinate can be extremely useful. With the aid of these diagrams, it is easy to rank mechanisms qualitatively and illustrate how changes in the leaving group, solvation, metal ion, steric bulk, etc. can move the minimum energy transition state along this mechanistic coordinate.

B. THE MECHANISTIC COORDINATE IN FREE ENERGY PROFILES OF SPONTANEOUS SUBSTITUTION REACTIONS

Figure 2 illustrates the qualitative use of a mechanistic continuum-free energy representation for defining I_a and I_d mechanisms of substitution reactions. The minimum in energy along the continuum of transition states for a particular set of reactants represents the mechanism with the highest probability of occurring. How-

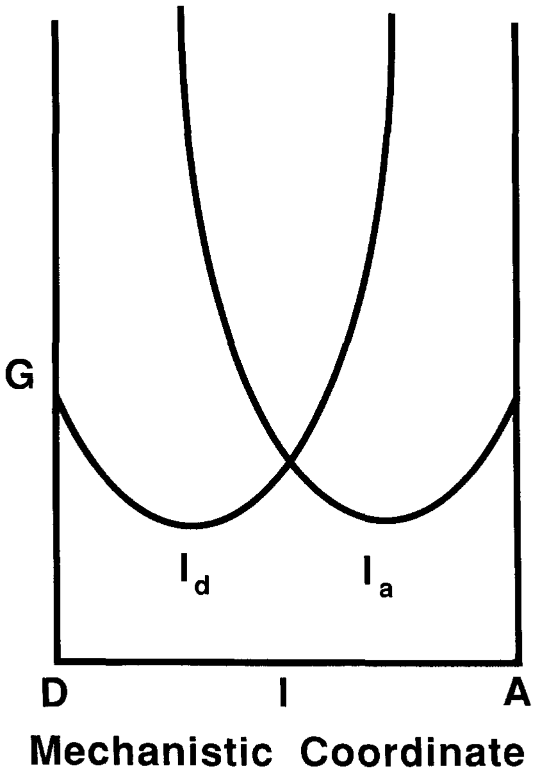


Fig. 2. Two-dimensional energy profile for the ground and transition states of an I_a and an I_d mechanism in terms of a mechanistic coordinate.

ever, there will be a slice of the continuum which will be energetically accessible, rather than the entire reaction occurring via the discrete mechanism that is represented by the minimum in the curve.

Such diagrams are not meant to be an accurate portrayal of the energies of the transition states, except for the Gibbs free energy of the lowest energy transition state, which is known from the kinetics of the reaction. At present, the available calculation methods are not sufficiently advanced to produce a three-dimensional free energy surface of transition states, although components of such surfaces have been calculated. In particular, quite sophisticated ligand field calculations have been performed on the stabilities of different transition states. The free energies have been calculated as a function of the degree of dissociation of the leaving group and the degree of association of the entering group [1,15,16]. However, they represent only one of three components that need to be considered simultaneously in order to make realistic calculations of the free energy surface of transition states. These are the ligand field contributions, steric contributions, and solvent contributions [2]. Some calculations of steric contributions to the stabilization of transition states have been performed [17], but they have not been used to produce an energy surface for the transition states. Solvent effects have not been considered, in a semi-quantitative fashion, until recently [2]. Despite the lack of reasonably accurate calculations of the energy surface of the transition states that incorporate all of these factors, qualitative and semi-quantitative predictions about the way in which the energy of the minimum transition states will be affected by their combined influences can be made and are discussed in the following sections.

C. THE EFFECTS OF ELECTRONIC CONFIGURATION AND METAL–LIGAND BOND LENGTHS ON THE SPONTANEOUS AQUATION REACTIONS OF HEXAAMMINEMETAL(III) COMPLEXES

Often it has been argued that the mechanisms of spontaneous aquations of transition metal complexes will be influenced chiefly by the d-electronic configuration and the length of the M–L bond lengths. Those complexes having a partially empty non-bonding t_{2g} subset of orbitals, and a larger relative size, are expected to be more susceptible to nucleophilic attack. Thus, the d^3 complex, $[Cr(NH_3)_6]^{3+}$ [18], and the d^5 complex, $[Ru(NH_3)_6]^{3+}$ [2,19] almost certainly undergo spontaneous aquation reactions via I_a mechanisms, whilst the d^6 complex, $[Co(NH_3)_6]^{3+}$, undergoes aquation via an I_d mechanism [2]. Therefore, the mechanistic profiles of the substitution reactions of $[Co(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ can be represented by the profiles in Fig. 2. The minimum in these energy profiles is not meant to be an accurate representation of where the mechanism lies, but is more an indication of the concepts that are involved. The smaller amount of steric strain required to form a seven-coordinate transition state in the larger $[Ru(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ ions will also favour I_a mechanisms as opposed to an I_d mechanism for the smaller $[Co(NH_3)_6]^{3+}$ ion. It is difficult to ascertain whether the steric or electronic factors are the most important in influencing the mechanistic differences [2].

In order to illustrate a trend down a group, the mechanisms of the substitution reactions of $[M(NH_3)_6]^{3+}$ (M = Co, Rh, Ir) are considered. In terms of electronic configuration, none of these ions should favour the formation of a seven-coordinate transition state. However, a lone pair of an incoming nucleophile could form a bond by interacting with the lowest level of unoccupied d-orbitals (i.e. 4d for Co, 5d for Rh and 6d for Ir). These unoccupied d-orbitals become more energetically accessible on going down the group. Therefore, the minimum energy transition state will tend to be less dissociated when going down the group. In addition, the substantial increase in M–N bond lengths on going from Co(III) to Rh(III) to Ir(III) (Co–N(av) = 1.961(4) Å, while the average M–N distances in $[M(NH_3)_6](CF_3SO_3)_3$ are 2.069 Å (Rh) and 2.091 Å (Ir) [20–22]) will make the formation of a seven-coordinate transition state more favourable for Rh(III) and Ir(III), compared with Co(III) [2,8–11,14]. The effects of these two factors are illustrated in Fig. 3. Note that, although both Rh(III) and Ir(III) are expected to be more associative than Co(III) in their minimum energy mechanisms, all are likely to undergo reactions in the I_d region of

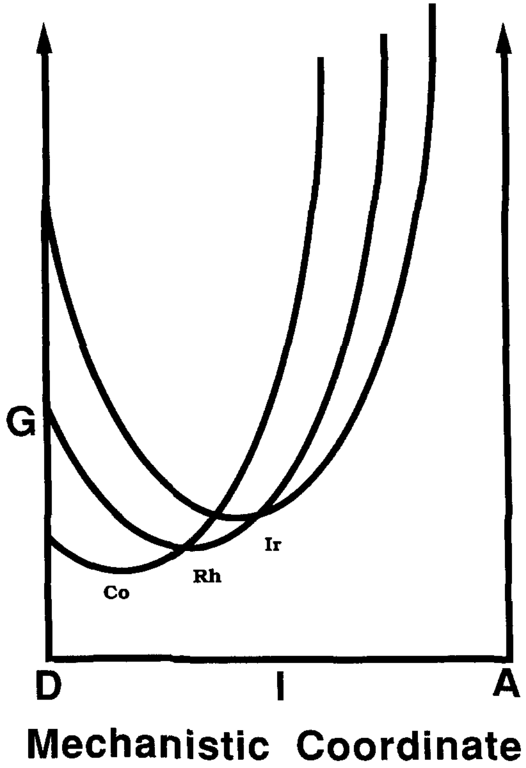


Fig. 3. Two-dimensional energy profile for the effects of the energy of the LUMO t_{2g} set of d orbitals and the M–N bond lengths on the mechanisms of substitution reaction of $[M(NH_3)_6]^{3+}$ (M = Co, Rh, Ir).

the continuum (or at least near the centre of such a continuum for Rh(III) and Ir(III)). Using the definitions of Langford and Gray, this is likely to place the mechanisms of substitution of these two complexes either within or near the definition of I_a. This highlights the problems that can arise if care is not taken in elaborating the definition that is used when describing a substitution mechanism in terms of I_a or I_d.

D. MECHANISMS OF THE SPONTANEOUS AQUATION REACTIONS OF PENTAAMINECHLOROMETAL(III) AND RELATED COMPLEXES

Many researchers working in the area of inorganic substitution reactions have assumed that the types of electronic and steric arguments used in the previous sections also apply to other complexes of the same metal ions, or at least to those with the same metal ion and non-reacting ligands. The latter has been the tenor of the recent review by Mønsted and Mønsted [1]. However, this has long been recognized not to be the case in S_N substitution reactions about carbon, where the mechanism can change from an S_N2 to an S_N1 mechanism, depending on a number of factors [14]. In particular, inorganic chemists often state that Cr(III) complexes undergo substitution reactions via I_a mechanisms or that they are associatively activated. From recent chemical information [3–6,23–25], and with the aid of the free energy profiles described above, it is easy to illustrate that the majority of aquation reactions that have been studied for M(III) complexes are likely to occur via mechanisms that fall in the I_d region of the mechanistic continuum. In all probability, for many substitution reactions the nature of the leaving group and solvation effects have larger influences on the mechanism of a reaction than do the electronic configuration, the size of the metal ion and the nature of the non-reacting ligands [2]. To illustrate this point, an analysis of the kinetic evidence that is available for the aquations of the $[M(NH_2R)_5Cl]^{2+}$ ions will be discussed in detail, and will be contrasted with the viewpoints put forward in the review of Mønsted and Mønsted [1]. Similar arguments are applicable to other systems containing a charged leaving group [2].

(i) π-Bonding perturbations of the mechanisms

It has been shown from studies of the X-ray crystal structures of the isomorphous series of complexes $[M(NH_3)_5Cl]Cl_2$ (M = Cr, Ru, Os, Co, Rh, Ir) that M–Cl π-bonding is more important for the d^3 and d^5 electronic configurations, in comparison with the d^6 electronic configuration [3]. While this is in line with chemical expectations, it does not appear that the effects of such π-bonding have been addressed, until recently, in terms of the effect on the mechanism [2,4–6,23–25]. In the case of the Cr, Ru and Os complexes, the quite strong M–Cl π-bonding, means that the orbitals that were available for the formation of a bond with an incoming nucleophile in the hexaammine complexes are now already involved in bonding. Therefore, on energetic grounds, they are less available for binding an incoming nucleophile and the Cr centre is much less electrophilic. Hence, arguments that justify an I_a mechanism on the basis of electronic configuration are less valid when the leaving group is involved in substantial π-bonding with the metal ion [2,5].

The other factor that arises due to π-bonding is the influence of steric effects on the stability of a seven-coordinate transition state. The steric requirements of the M–Cl multiple bond are such that the average N–M–Cl bond angle is increased beyond 90° for Cr(III), Ru(III) and Os(III), while it is less than 90° for Co(III), Rh(III) and Ir(III) in the isomorphous series discussed previously [3]. Thus, the greater steric requirements of the M–Cl multiple bonds more than negate the increases in M–N bond lengths (in terms of the steric hindrance involved in forming a seven-coordinate transition state). The net effect is that the minimum energy mechanism is moved along the mechanistic coordinate towards an I_d mechanism for Cr(III), Ru(III) and Os(III) by the inclusion of π-bonding considerations, as shown qualitatively in Fig. 4 for Cr(III). Since π-bonding for Co(III) is much less significant, there will be little effect on the mechanism for Co(III). In general, the effect of π-bonding on the

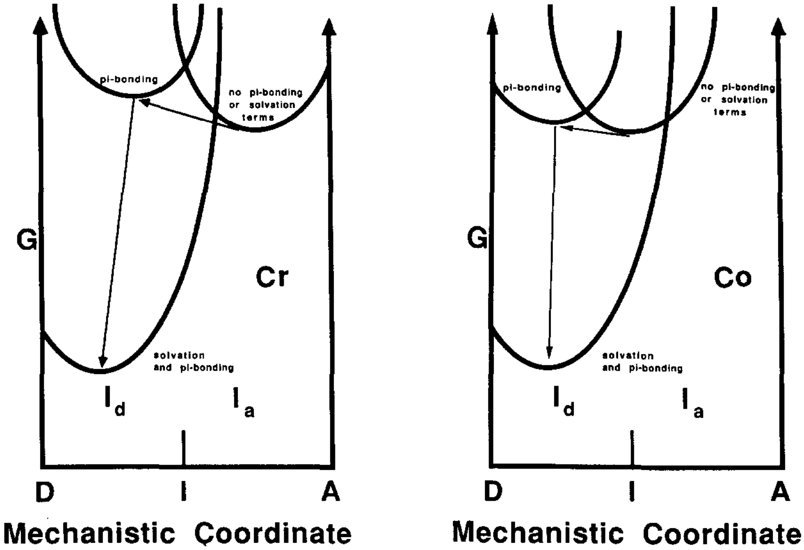


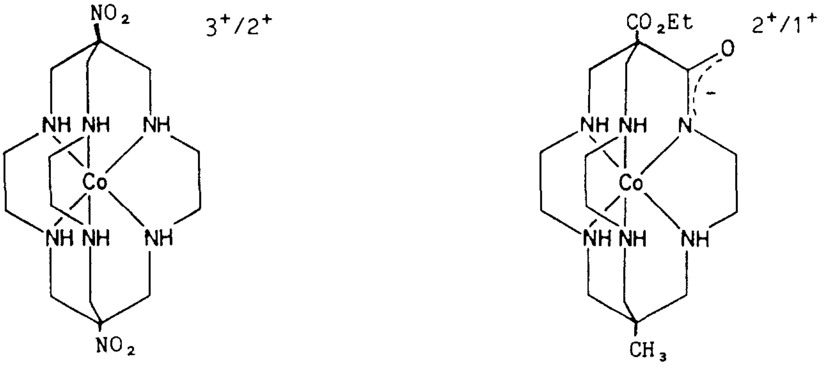
Fig. 4. Two-dimensional energy profile for the effects of π-bonding and solvation on the mechanisms of aquation of $[M(NH_3)_5Cl]^{2+}$ (M = Co and Cr).

substitution mechanisms of $[M^{III}(NH_3)_5X]^{n+}$ complexes, compared with $[M(NH_3)_6]^{3+}$ complexes, is to stabilize a more dissociated transition state in the minimum energy pathway as the strength of M–X π-bonding increases. This shift in the position of minimum energy pathway along the mechanistic continuum also increases on descending the Co group, but not to such a significant extent as for the d^3 and d^5 electronic configurations [2,3,6,25].

It has been erroneously claimed by Mønsted and Mønsted [1] that our analyses of π-bonding effects [3] are flawed. Their assertion is based on the large variations in M–Cl bond lengths that are reported in the literature, even for salts with the same complex ion [1]. These variations are due to a combination of packing forces and the variations in precision of the structure determinations. However, such analyses are not relevant to our work for the following reasons. Firstly, our studies have been with an isomorphous series of complexes, in which variations in crystal packing forces are kept at a minimum, i.e. structural changes within the series predominantly reflect inherent inner-sphere contributions of π-bonding, and not variations in outer-sphere interactions. Secondly, the structures that we have determined are very precise, with the standard deviations in the M–Cl bond lengths being 0.001 or 0.002 Å. Therefore, the precisions of the experiments are such that the variations in M–Cl bond lengths are much larger than the errors in their determinations. Thirdly, when we determined a second precise structure for a $[Ru(NH_3)_5Cl]^{2+}$ complex, with quite different packing forces, $[Ru(NH_3)_5Cl]Cl_{1.5}(BF_4)_{0.5}$ [23], the Ru–Cl bond lengths of both complexes were determined to be the same within experimental error. We believe that this is likely to be a general situation, i.e. when precisely determined crystal structures containing the same complex ions are compared, variations in M–Cl bonds will be small, irrespective of packing forces.

(ii) Solvent effects on the mechanism

In a limiting dissociative mechanism, the free energy of solvation of the pentacoordinate intermediate, $[M(NH_3)_5]^{3+}$, is estimated to be ~ 100 kJ mol^{-1}, while that of the ground state, $[M(NH_3)_5Cl]^{2+}$, is estimated to be ~ 60 kJ mol^{-1}. Such estimates are made from the calculated single-ion solvation energies of the cage complexes (Fig. 5) $[Co((NO_2)_2\text{-sar})]^{3+}$, **I**, and $[Co(CO_2Et,CH_3\text{-oxosar-H})]^{2+}$, **II** [26–28]. The total solvation energies do not appear to vary widely for a range of Co(III/II) amine couples or between $[Ru(en)_3]^{3+/2+}$ (en = 1,2-ethanediamine) and $[Ru(NH_3)_6]^{3+/2+}$. Therefore, the assumption that the total solvation energies of the ammine complexes and their cage complex analogues are similar is likely to be reasonable [26–28]. Even if there are substantial errors in this assumption, they will not have a large effect on the semi-quantitative arguments that are presented here, because they are dominated by solvation of the leaving group. The value of ΔG^0_{solv} for $Cl^-(g) \rightarrow Cl^-(aq)$ is -317 kJ mol^{-1} [29], therefore ΔG^0_{solv} for the spontaneous aquation reaction is of the order of -350 to -400 kJ mol^{-1} (Fig. 6). Indeed, because of an unfavourable equilibrium, the reaction would not occur to any significant extent if it were not for these very large solvent terms that drive the chemical reaction. The importance of such solvent terms in affecting the rate constants of aquation reactions has been recognized for a long time [30], but this appears to be the first



I

II

Fig. 5. Cage complexes used in studies of single-ion solvation. **I**, $[Co((NO_2)\text{-sar})]^{3+}$ = (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)cobalt(III). **II**, $[Co(CO_2Et,CH_3\text{-oxosar-H})]^{2+}$ = {1-ethyl formato-8-methyl-2-oxo-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosan-3-ato(1-)}cobalt(III).

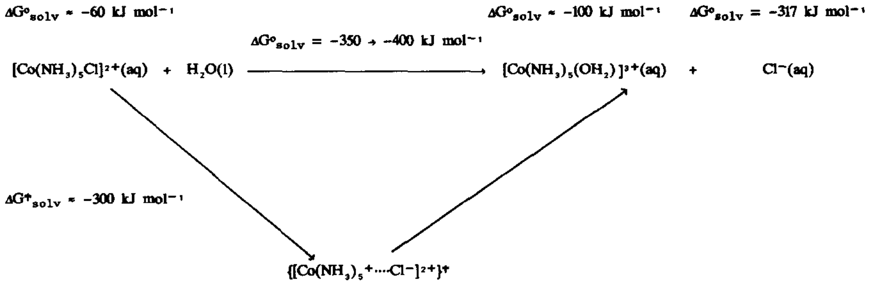


Fig. 6. Solvational energy terms in the spontaneous aquation reaction of $[Co(NH_3)_5Cl]^{2+}$.

instance where such a semi-quantitative analysis has been undertaken. A number of examples of the importance of solvation in driving substitution reactions involving charged leaving groups are given in a recent review [31]. The incorporation of similarly large solvation energy terms in the activation of the M–Cl bond is a necessary condition for the reaction to occur at a reasonable rate. It is clear that the only way that this can be achieved is through an I_d mechanism that is close to the dissociative limit, i.e. there is a very large discrimination for a charge-separated transition state (I_d mechanism) over one in which there is little charge separation (an I_a mechanism) [2].

In summary, the ground states of the reactants and products are both lowered in energy with respect to their gas phases by solvation, but the discrimination between the mechanisms is due to the effect of solvation on the energy of the transition states [2]. Thus, from purely electronic and size considerations, an I_a mechanism is favoured for the substitution reactions of the Cr(III) complexes. However, when the very large solvation energy terms and, to a lesser degree, π-bonding effects, are introduced, the activation barriers for I_d mechanisms become smaller than those for I_a mechanisms. The effects of these contributions on the mechanisms of the spontaneous aquation reactions of $[M(NH_3)_5Cl]^{2+}$, where M = Co(III) and Cr(III), are also illustrated in Fig. 4. This situation does not apply in the case of the substitution reactions of hexaammine complexes, where the leaving group is neutral and solvation energy contributions to the mechanisms are small [2,5,6]. The importance of solvation energy terms was recognized in the review by Mønsted and Mønsted [1], but they appear to have ignored what effect these solvation energy terms will have on the preferred mechanism. They also cited the work of Lawrance et al. on the spontaneous aquation reactions of pentaammine and pentakis(methanamine) complexes of Cr(III) and Co(III) [32–35] as refuting our notion that the mechanisms of spontaneous aquations are similar. Contrary to the assertions of the original authors [32–35] and the reviewers [1], these arguments simply highlight the general lack of appreciation of the importance of solvation in determining the mechanism. Thus, on the basis of volumes of activation, it has been claimed that there are mechanistic differences between Co(III) and Cr(III) for complexes with uncharged leaving groups [1,32–35].

This contention is reasonable because solvation energy terms are relatively small with such leaving groups. However, these results have little bearing on the mechanisms of substitution of the chloro complexes, where the solvational effects are much more important than the electronic configuration and/or the size of the complex in determining the mechanism. It is also apparent that the differences in $\Delta V^{\ddagger}$ between analogous Co(III) and Cr(III) complexes with neutral leaving groups are small [32–35] when compared with the volumes of activation that are expected for limiting A and D mechanisms [8–10]. Therefore, while the spontaneous aquation reactions of Cr(III) and Co(III) with uncharged leaving groups probably fall into the I_a and I_d regions of the mechanistic continuum, respectively, it appears that the mechanisms are similar and lie close to the true I mechanism, i.e. there is a similar degree of bond making and bond breaking in the transition state.

By invoking the concept of microscopic reversibility, such analyses show that the anation reactions of $[M(NH_2R)_5(OH_2)]^{3+}$ complexes by Cl^- must also belong to the family of I_d mechanisms. The reason for this lies in the solvation energy terms, because the formation of a seven-coordinate transition state will require a large amount of energy in terms of that required to partially desolvate $Cl^-(aq)$ which, in turn, will increase $\Delta G^{\ddagger}$. By contrast, an I_d mechanism near the dissociative limit will only involve small changes in the solvation energy terms because the leaving group (OH_2) has no charge [2].

Therefore, the driving forces for I_d mechanisms, which are probably near the dissociative limit for both the spontaneous aquation reactions of $[M(NH_2R)_5Cl]^{2+}$ and the spontaneous anation reactions of $[M(NH_2R)_5(OH_2)]^{3+}$, is the solvation energy of the Cl^- ion. It follows that the mechanism of substitution reactions of these complexes, and in particular the Cr(III) complexes, will become more associative in solvents that are less able to solvate Cl^-. However, such solvents will also favour the anation reaction; therefore, Cl^- substitution reactions will be difficult to measure because of both solubility problems and the fact that the equilibrium constant for the reaction

$$[M(NH_2R)_5Cl]^{2+}(solv) + solvent(l) \rightleftarrows [M(NH_2R)_5(solvent)]^{3+}(solv) + Cl^-(solv) \quad (1)$$

will lie very much to the left.

The importance of the nature of the solvent in determining the degree of charge separation in the transition state is another aspect that many researchers have failed to recognize. The very fact that the rate constants of solvation correlate with the ability of the solvent to stabilize a charge-separated transition state [31] indicates that the position of the minimum energy pathway on the mechanistic continuum is sensitive to the solvent.

The arguments presented in the preceding paragraphs imply the presence of a continuum of different mechanisms for the substitution reactions of $[Cr^{III}(NH_3)_5X]^{n+}$, ranging from an I_a mechanism for $X = NH_3$ (and other neutral leaving groups), to an I_d mechanism where X^{m-} is a strongly solvated leaving group. This is the likely reason for the different slopes of the plots of $\Delta G^{\ddagger}$ versus ΔG^0 found for the $[\mathrm{Cr^{III}(NH_3)_5X}]^{n+}$ and $[\mathrm{Co^{III}(NH_3)_5X}]^{n+}$ complexes [2], rather than being an indication of associative activation for all of the Cr(III) complexes, as compared with dissociative activation for all of the Co(III) complexes, as previously argued [1,36]. The reason why the slope of the line for Co(III) is near unity is that, even for a neutral leaving group, the mechanism falls in the $\mathrm{I_d}$ region of the mechanistic continuum (Langford and Gray, and Merbach nomenclatures). This is discussed in more detail elsewhere [2].

The similarities in the values of the volumes of activation for the spontaneous aquation reactions of the $[\mathrm{M(NH_3)_5Cl}]^{2+}$ (M = Co(III), Cr(III) and Rh(III) [37–40]), and the other activation parameters are also consistent with a similar mechanism applying for each of the metal ions [2,5].

(iii) Steric effects on the mechanism

In the past, the effects of steric bulk on the kinetics of spontaneous aquations of $[\mathrm{M(NH_2R)_5Cl}]^{2+}$ complexes (M = Co(III), Cr(III), Rh(III)) has also been taken as convincing evidence that the mechanism is different for the three metal ions. All factors being equal, it is expected that the addition of steric bulk will inhibit an associative interchange mechanism and accelerate a dissociative interchange mechanism. Since the former effect was observed for Cr(III) [37,41,42] and the latter for Co(III) [37,43,44] (Table 1), this has been taken as convincing evidence for mechanistic differences between the substitution reactions of these two metal ions. The rate constants for the substitution reactions of the Rh(III) analogues show very little change with increased steric bulk [45,46]. We have argued that the reason for the different kinetic behaviours that are observed for Co(III), Cr(III) and Rh(III) on the addition of steric bulk is a ground state effect due to changes in π-bonding. When this is considered, the mechanism is expected to be virtually the same in each case

TABLE 1

Crystallographic M–Cl bond lengths for $[\mathrm{M(NH_2R)_5Cl}]^{2+}$ ions in $[\mathrm{M(NH_2R)_5Cl]Cl_2}$ and values of the rate constants at 25°C for the spontaneous aquation reactions of the $[\mathrm{M(NH_2R)_5Cl}]^{2+}$ ions

Metal ion	$\mathrm{NH_3}$		$\mathrm{NH_2CH_3}$	
	M–Cl (Å)	10^6 k[a]	M–Cl (Å)	10^6 k[a]
Cr(III)	2.327(1)[b]	8.70[e]	2.299(1)[h]	0.261[e]
Co(III)	2.286(2)[c]	1.72[f]	2.283(1)[i]	39.6[f](34.0[k])
Rh(III)	2.356(1)[d]	0.038[g]	2.339(1)[j]	0.022[g]

[a]25°C. [b]Ref. 3. [c]Ref. 48. [d]Ref. 49. [e]Ref. 41. [f]Ref. 37. [g]Ref. 45. [h]Ref. 47. [i]$[\mathrm{Co(NH_2CH_3)_5Cl](NO_3)_2}$, Ref. 47. [j]Ref. 6. [k]Ref. 43.

[2,4–6,23–25]. This was ascertained from the variations in the M–Cl bond lengths in precisely determined X-ray structures (Table 1) [2,3,6,23–25,47–49]. Thus, the retardation of the rate of aquation of $[Cr(NH_2CH_3)_5Cl]^{2+}$, in comparison with $[Cr(NH_3)_5Cl]^{2+}$ is highly likely to be a ground state effect. It arises from the extra energy required to stretch the Cr–Cl bond in the pentakis(methanamine) complex in comparison with the pentaammine complex [2,4,5]. This analysis has been criticised by Mønsted and Mønsted [1], who stated that the solid state structures are not relevant to those in solution, and they have implied that we have not considered the ground state in solution. This is not so, since a substantial part of our original article [5] was devoted to a consideration of the solution structure and the effects of solvation on the mechanism. We have made an analysis of the ligand field spectra of the complexes in solution, which indicate that similar bond length considerations are applicable to the solution structures [5]. This has been further substantiated by recent IR evidence in which the solid state IR spectra of $[M(NH_2R)_5Cl]Cl_2$ have been compared with those obtained from methanolic solutions of $[M(NH_2R)_5Cl]^{2+}$ [50]. From these studies, it is clear that the trends in the M–Cl bonding are the same in both the solid state and in solution.

A further point which supports the notion that the structures that are observed in the solid state are maintained in solution are the activation parameters themselves. Thus, the similar values of $\Delta H^\ddagger$ observed for $[M(NH_3)_5Cl]^{2+}$ (M = Co(III) and Cr(III)) are somewhat surprising given that ligand field effects are less important in stabilizing the ground state towards substitution for Cr(III), in comparison with Co(III), irrespective of the mechanism. This is a strong indication of the importance of π-bonding stabilization of the Cr–Cl bond, with respect to the Co–Cl bond. Similarly, the much larger value of $\Delta H^\ddagger$ for the spontaneous aquation of $[Cr(NH_2CH_3)_5Cl]^{2+}$, when compared with $[Co(NH_2CH_3)_5Cl]^{2+}$, is consistent with the enhanced π-bonding in the chloropentakis(methanamine)chromium(III) complex if both complexes undergo aquation via I_d mechanisms.

Finally, it should be emphasized that we have made our assessments of the importance of the ground state effects on the basis of precisely determined structures. Other workers have had similar success in correlating bond lengths between the leaving group and reaction centre with the rates of substitution [51,52]. It is our belief that, if one works with precise structures and makes comparisons between isomorphous series, then the deductions made about solution reactivity from the solid data are entirely valid. However, care needs to be taken in assigning absolute rate constants on the basis of M–Cl bond lengths observed in the solid state. This is because of the previously enunciated importance of solvation contributions to the kinetics of substitution. Such problems will be particularly acute when comparing complexes of different charges, e.g. $[M(NH_3)_5Cl]^{2+}$ and $[M(NH_3)_4Cl_2]^+$. Here, the transition state solvation energies will be more important for the pentaammine complex, giving rise to greater reactivity for similar M–Cl bond lengths. Therefore, with the above caveat, the use of the differences in the M–Cl bond lengths between an isomorphous pentaammine series and an isomorphous pentakis(methanamine) series of complexes is an entirely valid way to rationalize the differences in reactivities. Although twinning problems [25,47] have prevented a precise determination of the structure of $[Co(NH_2CH_3)_5Cl]Cl_2$ as yet, we believe that the Co–Cl bond length will be very similar to that observed in the structure of $[Co(NH_2CH_3)_5Cl](NO_3)_2$ [47]. We base our prediction on the fact that, in the two precisely determined structures of $[Ru(NH_3)_5Cl]^{2+}$, where quite different packing forces were present, the Ru–Cl bond lengths were the same within the very small experimental error of the determinations [3,23]. It is likely to be a more common situation than is generally believed. Evidence to support this notion is the success of the Marcus–Hush theories of outer-sphere electron transfer [53–55] in predicting the order of magnitude of electron self-exchange rate constants. A major component of these calculations involves the incorporation of the difference in the metal ligand bond lengths between the two oxidation states of the redox couple. These differences are obtained from X-ray structures in the solid state (see, for example, refs. 22, 56 and 57). Generally, the solid state X-ray data that are used in these calculations to explain the rates of electron self-exchange reactions are much less precise than those which we have used in our work. However, the success of the modelling of electron transfer rate constants using such data is a strong indication of the validity of the approach that we have adopted.

It has been noted by others [37] that, due to the need to relieve steric strain in the transition state, the introduction of steric bulk in $[M(NH_2R)_5Cl]^{2+}$ will make the preferred mechanism more dissociative in comparison with $[M(NH_3)_5Cl]^{2+}$. This effect is illustrated semi-quantitatively in Fig. 7 for the aquation of $[Cr(NH_2R)_5Cl]^{2+}$ ($R=H$, CH_3). As outlined in the previous paragraphs, all the evidence now points to the minimum energy transition state for $R=H$ being in the I_d section of the mechanistic continuum. Therefore, the effect of the addition of steric bulk will be merely to move the minimum-energy mechanism further towards the dissociative limit. This is contrary to previous arguments [37], which have claimed that it results in a change-over from an I_a to an I_d mechanism.

(iv) Other effects of the ancillary ligands

The ancillary ligands can effect the mechanisms of substitution reactions in a number of ways, which can be additive or may tend to cancel out. In this section, the differences in the substitution behaviours of the pentaammine and pentaaqua complexes will be used to illustrate the point that there are a number of competing factors which will influence the mechanism when the ancillary ligands are changed. The first factor that needs to be considered is the effect of π-bonding, since the ammine ligand has no tendency to π-bond with the metal ion (except perhaps by hyperconjugation), whereas the aqua ligand undergoes π-bonding with M(III) ions [58]. Therefore, π-bonding of the leaving group to the metal centre in pentaaqua

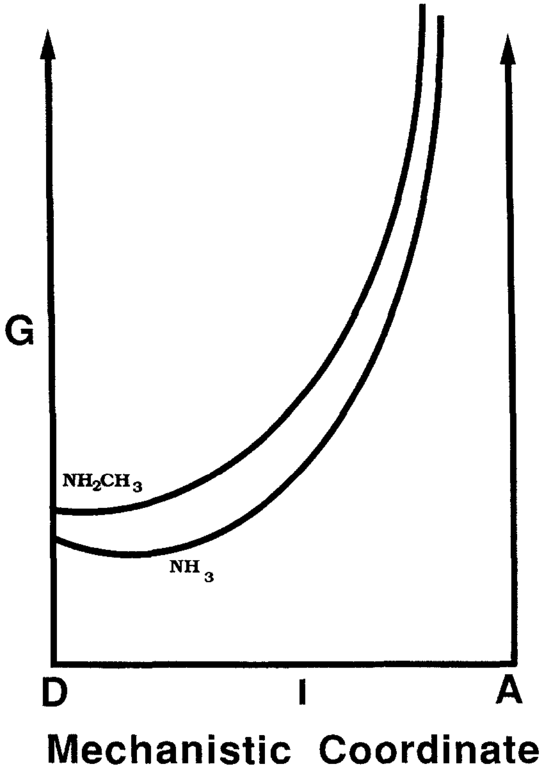


Fig. 7. Two-dimensional energy profile for the effects of steric bulk and π-bonding on the mechanism of aquation of $[Cr(NH_2R)_5Cl]^{2+}$; (a) R = H; (b) R = CH_3.

complexes, where there will be competition for π-bonding between the ancillary ligands and the leaving group, is expected to be weaker than in pentaammine complexes. The fact that the d orbitals are involved in π-bonding and hence less energetically available for forming a bond with an incoming nucleophile, will favour an I_d mechanism. Opposing this is the weaker π-bonding of the leaving group which is expected to make the substitution reactions of pentaaqua complexes more associative than the corresponding pentaammine complexes. Another important factor that will influence the mechanism is the steric factor. The aqua complexes have shorter M–ligand bonds and less non-bonding interactions than the ammine complexes [6,20–22,59,60], and the aqua ligands will undergo stronger hydrogen bonding with the incoming nucleophile (either water or an anion) than the ammine ligands. Therefore, the closer proximity of the incoming nucleophile to the metal centre in the ground state will make a seven-coordinate transition state more energetically accessible in the pentaaqua complexes, as opposed to the pentaammine complexes. A further complication is that the pentaaquametal(III) moiety will be more strongly solvated than the pentaamminemetal(III) moiety in a charge-separated transition state. This will tend to make the substitution reactions of the aqua complexes more dissociative than the ammine complexes. Given the variety of competing influences on the mechanisms when the ancillary ligands are changed, it is difficult to predict how these changes will influence the mechanism. However, the latter factor, in particular, will tend to cause a larger spread in the mechanisms of substitution reactions with changes in leaving group, due to the greater influence of solvation in stabilizing a charge-separated transition state. This may explain the lower slope of the $\Delta G^{\ddagger}$ versus ΔG^0 plot for the aquation reactions of $[\mathrm{Cr^{III}(OH_2)_5X}]^{n+}$, in comparison with that obtained for analogous $[\mathrm{Cr^{III}(NH_3)_5X}]^{n+}$ complexes [2]. Previously, this was argued as being due to the aqua complexes being more associative in their mechanisms than the ammine complexes [1]. However, the mechanisms of aquation of the pentaaqua Cr(III) complexes are likely to range from an $\mathrm{I_a}$ mechanism, in the case of aqua exchange in $[\mathrm{Cr(OH_2)_6}]^{3+}$ [8,9], to an $\mathrm{I_d}$ mechanism for the aquation of $[\mathrm{Cr(OH_2)_5Cl}]^{2+}$ [2] and similar complexes. Indeed, the mechanism for the latter may be closer to the dissociative limit than that for $[\mathrm{Cr(NH_3)_5Cl}]^{2+}$, due to the increased importance of the solvent stabilization of a dissociative mechanism for the pentaaqua complex. By contrast, the $\Delta V^{\ddagger}$ data provides strong evidence that the mechanism of solvent exchange is more associative for $[\mathrm{Cr(OH_2)_6}]^{3+}$ than $[\mathrm{Cr(NH_3)_5(OH_2)}]^{3+}$ [8,9]. This analysis also points to the problems of making blanket statements as to the degree of dissociation in the transition states of a series of related complexes on the basis of plots of ΔG^0 vs. $\Delta G^{\ddagger}$ [1]. Such an analysis fails to recognize that the mechanisms of individual complexes within the same series can be very different.

E. THE NUCLEOPHILIC STRENGTH OF THE ENTERING GROUP IN SUBSTITUTION REACTIONS OF AQUA COMPLEXES

For metal ions such as Cr(III), where the mechanism is sensitive to a number of factors, the nucleophilicity of the entering group also plays an important role in determining the mechanism. However, the ability of an entering group to act as an incoming nucleophile depends critically on the degree to which it is solvated, since solvent molecules will need to be displaced from around the nucleophile in order to form a seven-coordinate transition state. Therefore, much the same arguments apply as to the effect of the nucleophilic strength of the entering group as to the effects of solvent.

F. CONCLUSIONS

The statement made in the review by Mønsted and Mønsted [1] in referring to our original work [4–6] "... that it is not immediately obvious why differences in the transition state properties indicated by other criteria are disregarded" is not correct. Indeed, in our original articles [4–6], we addressed many of these criteria.

All the remaining criteria that have been used to assign mechanistic differences have been addressed here, or in another review [2]. When all of the data are examined on the basis of the new information on the ground state properties [3–6], there is no compelling evidence to support significant mechanistic differences between the spontaneous substitution reactions of the $[M(NH_2R)_5Cl]^{2+}$ complexes, at least for M = Co, Cr and Rh. By contrast, all of the evidence now supports similar mechanistic pathways for these reactions. As discussed in the previous sections, there are distinct mechanistic differences in the substitution reactions that involve neutral leaving groups. However, these differences cannot be applied to the substitution reactions where the mechanisms are dominated by the solvent contributions to stabilizing a charge-separated transition state. In summary, there are several points that are general to the analysis of the mechanisms of substitution reactions.

(i) The electronic structures and the sizes of the central metal ions are not as important in determining the mechanism as previously thought, but are only two of several important factors.

(ii) Solvation effects are likely to be the overriding factors in controlling the mechanism of substitution reactions with charged leaving groups.

(iii) The mechanisms of substitution reactions involving neutral leaving groups will be much more sensitive to the other factors, such as electronic configuration and size. They can vary widely over the mechanistic coordinate for analogous complexes with different metal ions.

(iv) The use of the mechanistic labels I_a and I_d is not as enlightening as the use of free energy–mechanistic coordinate diagrams, which illustrate the comparison of the relative positions of the mechanisms of substitution of related complexes in a qualitative fashion.

(v) The activation process for substitution reactions of metal ions, such as Cr(III), may vary over most of the mechanistic coordinate of interchange mechanisms, depending on a number of factors. For the case of aquations of Cr(III) complexes with charged leaving groups, such as Cl^-, the mechanisms almost certainly lie in the I_d region of the mechanistic continuum and near the dissociative limit (i.e. in the I_d region in both the Langford and Gray and the Merbach terminology). However, other mechanisms can lie in the I_d(Merbach)/I_a(Langford and Gray) or the I_a(Merbach, and Langford and Gray) regions of the mechanistic continuum, depending on a number of factors. These include the natures of the leaving group, solvent, steric interactions, etc. The ambiguities and misconceptions that arise from the different nomenclatures, and the problems associated with compartmentalising a mechanistic continuum under the labels of I_a and I_d, can be alleviated by the use of the mechanistic continuum–free energy diagrams. The other solution to the dilemma is to avoid the terms I_a and I_d completely [12]. By the use of terminology such as the reaction proceeds by a mechanism in which bond breaking substantially proceeds bond making, etc., ambiguous terminology such as I_a or I_d can be avoided.

As a final comment, the recent work illustrates the point that it is not possible to prove a mechanism. It is only possible to deduce the most likely mechanism on the basis of the experimental information that is available at the time. Prior to our recent work [3–6], the arguments contained in the review of Mønsted and Mønsted, and others, provided fairly convincing evidence of mechanistic differences in the kinetics of substitution of chloro complexes of Co(III), Cr(III) and Rh(III). However, in hindsight, when the ground states of the complexes are examined, and the effects of solvation are considered, all the previous mechanistic assumptions evaporate. This shows the desirability to have a knowledge of these factors in making mechanistic conclusions. Too often in the literature, mechanistic conclusions are made, and stated as fact, on the basis of limited kinetic information. The work presented in this review shows that, even for systems that have been studied in a considerable amount of detail, new results can change completely the way in which previous data are interpreted.

ACKNOWLEDGMENTS

I am grateful to Alan M. Sargeson for helpful discussions and to James K. Beattie and Trevor W. Hambley for providing information on M–N bond lengths prior to publication. I also wish to acknowledge the support of the Australian Research Council for partially funding some aspects of this work.

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