Coordination Chemistry Reviews, 14 (1974) 217–268

ACTIVATION PARAMETERS AND REACTION MECHANISM IN OCTAHEDRAL SUBSTITUTION

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(Received March 20th, 1974)

CONTENTS

A. INTRODUCTION

Inorganic chemistry seeks to achieve a comprehensive understanding of how and why the chemistries of the various elements differ from one another. The essence of a great many important and intriguing chemical phenomena is reaction kinetics (witness the vast numbers of coordination compounds of chromium(III) and spin-paired cobalt(III) which can be isolated by virtue of the slowness of their substitution reactions), and understanding of the kinetics depends in turn upon the use of appropriate mechanistic models.

Unfortunately, the pursuit of reaction mechanisms has tended to become an end in itself, sometimes tending toward mediaeval scholasticism. The present article seeks instead to achieve some degree of rationalization of the kinetic phenomena, using as guidelines some simple mechanistic models based on current concepts of the nature of dissolved inorganic species. Mechanistic models are considered to have scientific value only if they can be conceived of as affecting the rate or course of a reaction in some clearly recognizable and characteristic way. In particular, it will be argued that if one adopts as a working hypothesis the view that *cationic octahedral complexes* of cobalt(III) normally undergo simple ligand substitution by a *dissociative interchange* mechanism, while for analogous complexes of other *trivalent* transition metals the mechanism is *associative interchange*, then the course, kinetic characteristics and stereochemistry of these reactions can be rationalized.

We are not presently able to calculate reaction rates in condensed phases absolutely. Consequently, the discussion must centre around relative rather than absolute quantities; that is, we shall be concerned primarily with the *systematics of activation parameters* for selected series of comparable reactions, and these will be used as a framework for the introduction of other material. Attention will be confined to octahedral substitution, mainly with reference to systems for which sufficient data of the kind and accuracy required are available; this article is therefore selective and not comprehensive. The reader is referred to the several excellent monographs on inorganic reaction mechanisms that have appeared in recent years for further information and other viewpoints[1–7].

In the following, the solvent is water unless otherwise stated, and thermodynamic and extrathermodynamic quantities are referred to the standard state of unit molarity at 25°C, 1 atm and the prevailing ionic strength, rather than the conventional choice of unit molality at hypothetical infinite dilution.

B. MECHANISMS OF LIGAND SUBSTITUTION

The following concentric zones are generally considered to surround a metal ion of charge 2+ or more in water[7–9]: (*a*) the first coordination sphere, in which ligands are covalently bound to the central metal ion, as in $(H_2O)_6Cr^{3+}$; (*b*) a second coordination sphere or solvation sheath which may contain electrostatically retained anions (as an *ion-pair* or *ion-triplet*) or other foreign species in addition to numerous solvent molecules; (*c*) a region of transition to bulk solvent structure, and (*d*) bulk solvent. For cations of low charge/radius ratio such as K^+, and for many large anions such as I^- or ClO_4^-, which exert only a weak centrally orienting field on the solvent, zones (*a*), (*b*) and (*c*) may be indistinguishable, and the net effect of the presence of the ion will be a loss of pre-existing solvent structure.

However, for a cation with a strong central field in a protonic solvent such as water, hydrogen bonding by outwardly oriented protons of molecules in zones (*a*) and (*b*) may lead to the creation of a relatively well-ordered zone (*b*) several molecular layers deep. Thus, even though zone (*c*) will presumably be disorganized on account of the inevitable mismatch in structure between zone (*b*) and bulk solvent, the net effect of the presence of the ion on the solvent will be structure-making.

Thus, the replacement of X by Y in the first coordination sphere (c.s.) of a metal complex ML_5X must be preceded by the entry of Y into the second c.s., forming an "encounter complex"[4,7]. If Y is anionic, the water of solvation is evidently largely retained within this encounter complex (ion-pair) and is lost only when Y moves into the first c.s.[10]. In other respects, however, solvent exchange reactions (X = Y = solvent, in reaction (1)) may be seen to be simply special cases of ligand substitution — but important ones, since solvent molecules far outnumber other potential ligands in the second c.s., and so entering ligands Y must compete with solvent molecules for entry into the first c.s.

$$ML_5X + Y \rightarrow ML_5Y + X \tag{1}$$

Following Langford and Gray[4,7], but with some slight revisions of their definitions, we can anticipate three major mechanistic classes of heterolytic octahedral substitution reactions in solution.

Dissociative (D): the outgoing ligand X departs independently of the influence of Y, and the five-coordinate intermediate and its second c.s. lose all "memory" of X before the M—Y bond begins to form. This situation will be realized in two cases: (1) when ML_5 is long-lived relative to the timescale of exchange of potential ligands between the second c.s. and bulk solution; and (2) when X *cannot* be held in the second c.s. and passes immediately into bulk solution — as when X and ML_5 carry the same charge (e.g. $HgCl^+$ separating from $Co(NH_3)_5^{3+}$) or when X is uncharged and non-polar (e.g. N_2 loss after nitrosation of $Co(NH_3)_5N_3^{2+}$).

Associative (A): the incoming ligand Y forms a seven-coordinate intermediate ML_5XY which is long-lived in the above sense.

Interchange (I): exchange of X for Y occurs within a preassembled *encounter complex* $[\{ML_5X\}Y, xH_2O]$; M—Y bond-forming occurs before ML_5 has lost "memory" of X, that is, before the second coordination sphere has had time to relax. We can distinguish an *associative interchange* (I_a) mechanism, in which M—Y bond-making is essentially synchronous with M—X bond-making, giving a transient seven-coordinate intermediate ML_5XY which will reflect the properties of both X and Y but which will be sufficiently short-lived as to warrant identification with the transition state. Conversely, if bond-making by Y occurs only after the M—X bond is broken but before X is lost from the second c.s., we have a *dissociative interchange* (I_d) in which a five-coordinate intermediate ML_5 is created transitorily inside an assemblage (first and second c.s. taken together) of essentially fixed overall composition.

The distinction between I_d and case (2) of the D mechanism serves to emphasize that the salient feature of the I mechanisms is that X is still present in the assemblage when M—Y bond-making occurs. Thus, we might define the I processes as ones which take place before the second c.s. has had time to relax, it being understood that this relaxation time will depend to some extent on the natures of X, Y, ML_5 and the solvent. Solvation changes necessary for completion of the interchange amount to changes in the second c.s., so that the latter definition implies that solvent reorganization occurs prior to or after the rate-determining process, unless exchange of solvent between the second c.s. and bulk solution is much faster than the same movements of other X and Y species. The solvent content of the second c.s. will fluctuate with time about a mean solvation number; if a sufficient excess (or deficiency) of solvent is present in the second c.s. to trap X and release Y when a suitably aberrant molecular vibration occurs, net reaction will be observed — otherwise, the molecular configuration will snap back to its original state.

Bennetto and Caldin[11] propose a somewhat different model in which the movements of solvent and other species in the regions (*a*), (*b*), (*c*) and (*d*) are concerted. Our preferred view is that the presumed disorganization of the solvent in zone (*c*) effectively isolates zones (*a*) and (*b*) from external influences, on the timescale of the residence of species in the second c.s. An emphasis on the lifetime of five- or seven-coordinate intermediates relative to this timescale, as developed above, then leads to some significant predictions concerning relative rates and products of reactions.

Ironically, the original simple Ingoldian S_N1/S_N2 dichotomy, borrowed as such from organic chemistry but now generally recognized as being inadequate to describe reactions such as eqn. (1), has recently been discarded by some organic chemists[12] in favour of a classification similar to Langford's.

C. RATE LAWS

(i) Order with respect to solvent

Rate laws are governed by the stoichiometric reaction mechanism(s) inasmuch as the individual terms in the law reflect the composition of the pertinent transition states. However, since the solvent is usually present at near unit activity, it is unlikely to appear specifically in the empirical rate law even of solvolysis reactions, except under special conditions. As a rather extreme example, the aquation of $(H_2O)_5CrN_3^{2+}$ proceeds, in the pH range 0—3 and at constant ionic strength, according to the rate law[13—15]

$$-\mathrm{d}\ln[\mathrm{CrN_3}^{2+}]/\mathrm{d}t = k_1[\mathrm{H}^+] + k_0 + k_{-1}[\mathrm{H}^+]^{-1} + k_{-2}[\mathrm{H}^+]^{-2} \qquad (2)$$

which reflects the existence of *four* parallel reaction paths involving transition states of composition (exclusive of H_2O) CrN_3H^{3+}, CrN_3^{2+}, $Cr(OH)N_3^+$ and $Cr(OH)_2N_3^0$. At sufficiently high acidities, however, substantial fractions of the substrate are present as $(H_2O)_5CrN_3H^{3+}$, for which the acidity constant K_1 can be expressed in terms of the acidity function h_0 as

$$K_1 = [\mathrm{CrN_3}^{2+}]h_0/[\mathrm{CrN_3H}^{3+}] \qquad (3)$$

At the same time, the activity a_w of water becomes considerably reduced from unity because of the need to solvate the large amounts of hydrogen ion present[14]. The reaction proceeds entirely via the CrN_3H^{3+} intermediate under these conditions, and the rate law becomes

$$-\mathrm{d}\ln[\mathrm{CrN_3}^{2+}]/\mathrm{d}t = (k_2a_w + k_3)h_0/(K_1 + h_0) \qquad (4)$$

The term k_2a_w (which would account for ~ 94% of the reaction rate for the path characterized by k_1 at $a_w \sim 1$) may be taken to indicate the associative attack of H_2O on $(H_2O)_5CrN_3H^{3+}$ in the rate-determining step, while the term k_3 presumably represents the dissociative decay[14] of $(H_2O)_5CrN_3H^{3+}$. For the aquation of $(NH_3)_5CoN_3^{2+}$, a rate law involving terms in $[OH^-]$, $[H^+]$ and $[H^+]^2$ in addition to the pH-independent term has been reported[16], but the $[H^+]^2$ term evidently represents ionic strength effects on the term first-order in $[H^+]$.

The problem of reaction orders with respect to solvent is a difficult one to resolve, since any attempt to alter the solvent activity appreciably, e.g. by adding large amounts of some other solvent, leads to drastic changes in the structure, dielectric constant and other solvent properties, and introduces uncertainties concerning the relative distribution of the two types of solvent molecules between the second c.s. and the bulk solvent. King and his co-workers[17—24] have made considerable progress toward the elucidation of solvation and substitution processes at Cr^{III} centres in mixed aqueous solvents, but usually there remains some ambiguity concerning the order of reaction with respect to water (or the diluent). Langford and co-workers[25,26] and Frankel[27] have shown that information concerning the composition of the second c.s. of Ni^{II} and Cr^{III} in suitable mixed solvents is obtainable from NMR data, but even here care is needed in interpreting the results mechanistically; thus, for $Cr(DMSO)_6^{3+}$ (DMSO = dimethylsulphoxide) in DMSO—nitromethane mixtures, it appears that one DMSO is uniquely firmly held in the second c.s., so that, although DMSO ligand exchange is evidently associative[28], the exchange rate is essentially independent of solvent composition for the higher DMSO contents.

For our present purposes, then, it seems advisable to avoid these complications by concentrating on single-solvent systems with fairly low solute contents, and to consider the role of solutes Y in the rate law for eqn. (1) according to mechanistic type.

(ii) D and A mechanisms

Detailed considerations of the rate laws for D mechanisms and of their manifestations have been published recently[1,29,30], and need not be repeated here. At the simplest level, the kinetic consequences of a D mechanism are:

(*a*) That the dependence of d ln [L_5MY]/d*t* upon [Y] is first-order at low [Y], and zeroth-order at sufficiently high [Y] (corresponding to the trapping of *all* L_5M fragments by Y rather than by solvent or a competitor Y').

(*b*) That the limiting value of the d ln [L_5MY]/d*t* is the same for all Y.

(*c*) That —d ln [L_5MX]/d*t* is independent of the nature and concentration of Y.

Effect (*a*) is also to be expected for an I mechanism, if the fraction of L_5MX which forms an encounter complex (ion pair, etc.) {L_5MX, Y} becomes large at large [Y], and conceivably even for an A mechanism, if substantial fractions of L_5MX become complexed as L_5MXY in the pre-equilibrium step (an unlikely occurrence even for Pt^{II} complexes, which react by an A mechanism, and highly improbable for sterically congested octahedral species).

(iii) I mechanisms

For cationic ML_5X and anionic Y, ion pairing and the likely orientation of the solvating water molecules with the negative O end of the dipole toward the positive centre M make it highly unlikely that an ML_5 cation would survive for as long as the relaxation time of the second c.s. Thus, *substitutions of cationic complexes will almost inevitably be I rather than D*, and it is significant that most well-established cases of D behaviour are associated with anionic or neutral complexes[29], though it evidently can occur in cations subject to special effects such as the powerful *trans*-activation[30] by Cl in $Rh(OH_2)_5Cl^{2+}$. For an I mechanism, the change from first-order to zeroth-order dependence of d ln [L_5MY]/d*t* on [Y] reflects saturation of ion-pair formation, and the limiting value of d ln [L_5MY]/d*t* (= k_i) is the rate coefficient for the internal exchange of X for Y *within the ion-pair*

$$\mathrm{d}\ln[L_5MY]/\mathrm{d}t = k_iQ_{IP}[Y]/(1 + Q_{IP}[Y]) \qquad (5)$$

where Q_{IP} is the formation quotient for the ion-pair {ML_5X, Y}. This formulation, which was developed by Langford and Muir[31] for the $Co(NH_3)_5X^{(3-n)+}$ series, has been challenged recently by Burnett[32], who considers that the rate data should be interpreted with allowance for the possible involvement of ion triplets (some involving ClO_4^-), but Barber and Reynolds[33] have subsequently shown that the Langford—Muir treatment (eqn. (5)) is essentially correct.

(iv) I_a mechanisms

For the anation of ML_5OH_2 cations in water by anionic Y via an I mechanism, the rate of entry of Y into the first c.s. from the second can exceed the rate of exchange of coordinated water with solvent water (first-order rate coefficient k_{ex}) *only if* Y initiates the process of its own entry (i.e. if the mechanism is I_a) *and* if Y is a markedly better nucleophile toward M than is H_2O (bearing in mind that H_2O is always in large excess over Y in the second c.s.). This is likely to be realized when M is a class "b"[34] or "soft"[35] acceptor, in which case it would form better covalent links with Cl^-, I^-, etc. than with the typically "hard" base H_2O. I_a substitutions are anticipated for such substrates in any event[36], and indeed we find $k_i > k_{ex}$ for the anations of $Rh(NH_3)_5OH_2^{3+}$ (refs. 37, 38) and $Ir(NH_3)_5OH_2^{3+}$ (refs. 39, 40) by Cl^- (an associative mechanism for aquations of Rh^{III} haloammines was first suggested by Johnson et al.[41]; this is the microscopic reverse).

However, it is to be expected that, for classic class "a" acceptors such as Cr^{III} which display I_a behaviour in other respects (see below), k_i is likely to be less than k_{ex} for most Y, since water is a typical hard ligand and will be available in large excess over other Y. Possible successful competitors might be the hard ions F^-, NO_3^- and SO_4^{2-}, but the first introduces complications due to its Brønsted basicity[42] (discussed later) and the latter two tend to destroy Cr^{III} ammine complexes after coordination through *cis*-activation (probably by virtue of a proclivity to I_a ring closure)[43], so that definitive experiments likely to show $k_i > k_{ex}$ are difficult to realize for class "a" interactions in water. To date, the detailed application of eqn. (5) to Cr^{III} substitutions has been tried only for the anations of $Cr(NH_3)_5OH_2^{3+}$ by Cl^- and NCS^-, and for these $k_i \sim 0.02k_{ex}$ and $0.04k_{ex}$ respectively[44,45] at 29.7°C and ionic strength $I = 0.15$ M.

The data of Fogel et al.[46] for the anation of $(H_2O)_6Cr^{3+}$ by SO_4^{2-} at 45°C indicate that k_i is at least $0.6k_{ex}$ (ref. 47) but probably does not exceed k_{ex}. However, as Tobe[48] points out, the anations of $(H_2O)_6Cr^{3+}$ exhibit another feature expected of I_a mechanisms, viz. that k_i should vary widely as Y^{n-} is changed. For ion pairs of $(H_2O)_6Cr^{3+}$ with NCS^- and Cl^- at 25°C and $I \simeq 1$ M, Q_{IP} is about 1.0 and 0.9 M^{-1} respectively[49,50]. From these and the bimolecular rate coefficients k_{an} for the anation reactions calculated in the manner of Espenson[51] from our own compilation[52]* (25°C, $I \sim 1.0$ M), $k_i/k_{ex} = 0.6$, 0.01, 2×10^{-3} and (assuming Q_{IP} again ~ 1.0 M^{-1}) 3×10^{-4} for $Y^- = NCS^-$,

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* There are some discrepancies between the two sources, e.g. our calculations give 8.7×10^{-9} M^{-1} sec^{-1} for $Y = Br^-$ and 1.66×10^{-6} M^{-1} sec^{-1} for NCS^-.

Cl^-, SCN^- and I^- respectively. Thus, the nucleophilic powers of Y^{n-} toward $(H_2O)_6Cr^{3+}$ vary over more than a 10^4-fold range, from SO_4^{2-} and NCS^- to I^-. Tobe[48] stressed that, despite these results, "an I_a mechanism is not mandatory [for Cr^{III} centres] unless a plausible explanation of the very high competing nucleophilicity of solvent water is forthcoming", but the above hard/soft donor/acceptor argument provides at least a partial rationale.

(v) I_d mechanisms

For an I_d process, k_i must necessarily be less than or equal to k_{ex}, and, in the absence of special effects, k_i values should be rather similar for a variety of Y, since Y will be scavenged by ML_5 more or less on a statistical basis in competition with water. This is well illustrated by the anations of $Co(NH_3)_5OH_2^{3+}$, for which $k_i \simeq 0.2k_{ex}$ for a surprising variety[31] of Y (an apparent anomaly is $Y^- = N_3^-$, for which $k_i \simeq k_{ex}$, but here the mechanism seems to involve special hydrogen-bonding effects tantamount to HN_3 formation in the transition state)[53].

The above applications of eqn. (5) require that the value of k_{ex} used be that for solvent exchange by the complex *within an ion pair*, rather than k_{ex} for the free ion. Watts, in particular, has stressed that the ion-pair should be regarded as a new chemical species with properties that may differ from those of the free ions, and there is ample evidence (see, e.g. ref. 54 and citations therein) that ion-pairing *can* accelerate octahedral substitution to some extent[55]. However, for chloride and other ion-pairs with $M(NH_3)_5OH_2^{3+}$ (M = Cr, Rh, Ir)[37,39,40,44], k_{ex} has proved to be essentially the same as for free $M(NH_3)_5OH_2^{3+}$.

Non-aqueous solvents: Ion-pairing is much more marked in most non-aqueous solvents than in water[55], and behaviour according to eqn. (5) becomes very obvious, although ion-triplet formation can complicate matters. For replacement of DMSO in *cis*-$Co(en)_2NO_2(DMSO)^{2+}$ in DMSO solvent by $Y^- = NO_2^-$, Cl^- and NCS^-, k_i was about the same for all three Y^- and about $0.3k_{ex}$; again Co^{III} displays typical I_d behaviour[56]. For Br^- anation of *cis*- and *trans*-$Cr(en)_2Br(DMSO)^{2+}$ in DMSO, some degree of bond-making by Br^- seems to occur in the transition state[57], while, for anation of $Cr(DMSO)_6^{3+}$ in DMSO[58,59], $k_i \simeq 4k_{ex}$ for $Y^- = NCS^-$ and as much as $100k_{ex}$ for $Y^- = N_3^-$ (ref. 28); thus, Cr^{III} is exhibiting classic I_a behaviour, although Lo and Watts[59] consider that a case can still be made for an I_d mechanism.

(vi) Homolytic mechanisms

The foregoing considers only heterolytic M—X bond fission, but some homolytic decompositions of transition-metal complexes evidently occur even amongst aquo complexes in water. Thus, $HNC_5H_4CH_2Cr(OH_2)_5^{3+}$ seems to decay (in acidic O_2-free solution at temperatures > 30°) via a pre-equilibrium giving Cr^{2+} and $\dot{C}H_2C_5H_4NH^+$, the rate-determining first-order decay of the last species giving rise to overall *half*-order kinetics with respect to the substrate[60]. Other salient features of the rate law are a powerful retarding effect of added Cr^{2+} (in accordance with the existence of the pre-equilibrium) and the *lack* of dependence of the rate on $[H^+]$ in acidic solution[60,61], while the reaction products clearly support a radical mechanism[61]. If oxygen is present, the rate-controlling step becomes the Cr—C bond fission, and the kinetics become first-order in substrate. In retrospect, the recombination rate of Cr^{2+} and $\dot{C}H_2C_5H_4NH^+$ derived in ref. 60 seems unrealistically low (and is in fact inconsistent with the assumption of steady state kinetics), but the gross features of the mechanism are still clearly seen in the *form* of the rate law, the effect of Cr^{2+} and of O_2, and the nature of the products (with and without O_2).

By contrast, methyl- and several hydroxyalkylpentaaquochromium(III) species aquate via simple first-order paths *which exhibit strong* H^+ *catalysis*, and these facts (together with the magnitudes of ΔH^* and ΔS^*) point to rate-determining heterolysis involving a virtual carbanion[62]. Thus, homolysis is evidently unusual even in such bizarre compounds as these alkylpentaaquochromium complexes.

D. FREE ENERGIES OF ACTIVATION, ΔG^*

Kinetic and thermodynamic phenomena may be discussed together in compatible terms by application of transition state theory[63], according to which rate coefficients may be expressed as free energies of activation ΔG^* ($= -\ln kh/\kappa T$, assuming unit transmission coefficients). For metal complexes, it is well recognized that high thermodynamic stability in general is not necessarily correlated with kinetic inertness[64], but, within a series of related reactions proceeding by a common mechanism, it is reasonable to expect a correlation[65] between ΔG^* and ΔG^0. If G_{MX} and G_{MY} represent the free energies for the dissociation of the reactants $L_5MX + Y$ and the products $L_5MY + X$ respectively to $L_5M + X + Y$ (with appropriate solvation) and G^* is the instantaneous free energy of the system relative to the reactants as reaction proceeds from reactants to products, we can write

$$G^* = bG_{MX} - (1-c)\,G_{MY} \tag{6}$$

where b and c represent the fractional extents of M—X and M—Y bond formation (in terms of free energy). For the transition state, we write $G^* = \Delta G^*_{MX}$, $b = \beta$, and $c = \gamma$.

(i) Dissociative mechanisms

Figure 1 represents an I_d reaction profile. The two curves are analogous to Morse functions for the stretching and rupture of the L_5M—X and L_5M—Y

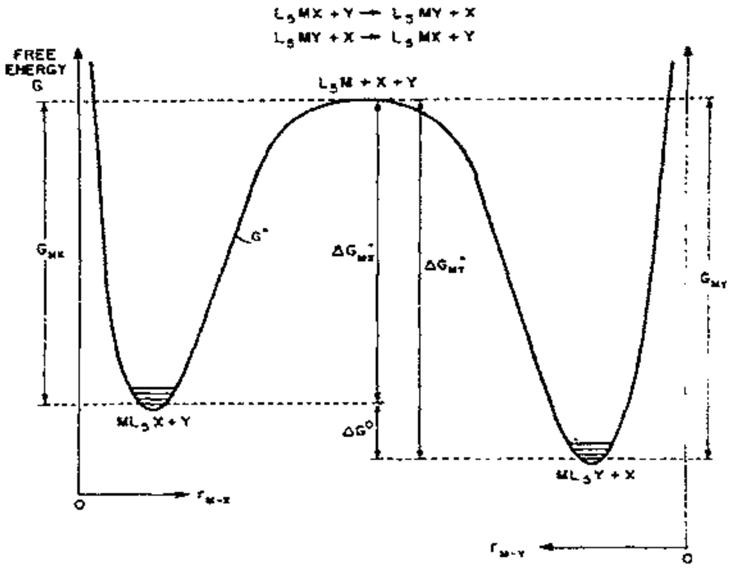

Fig. 1. Free-energy profile for an I_d mechanism.

bonds, except that they are presented here in terms of free energies and include appropriate solvation. If the mechanism were D, and the five-coordinate intermediate were long-lived as defined in Section B (case 1), a third free-energy trough would appear between the two complete pseudo-Morse curves, representing the intermediate L_5M. As the diagram is drawn, the level marked $L_5M + X + Y$ refers to these species assembled in an I_d encounter complex. Here we see that the presence of Y has no influence on ΔG_{MX}, and that $\Delta G^*_{MX} = G_{MX}$.

$$\Delta G^*_{MX} = G_{MX} = G_{MY} + \Delta G^\circ \tag{7}$$

Thus, for a series of reactions with the same Y, we have constant G_{MY} and a linear free energy relationship (LFER) of unit slope; that is, in the Brønsted relationship

$$\Delta G^* = \alpha \Delta G^\circ + \text{constant} \tag{8}$$

we have for the Brønsted slope

$$\alpha = (\partial\ \Delta G^*/\partial\ \Delta G^\circ)_{P,T} = 1.0 \tag{9}$$

In simple terms, the existence of an LFER of $\alpha = 1.0$ means that the rate coefficient for the *reverse* reaction is essentially the same for all X, because the equilibrium quotient is the quotient of the rate coefficients of the forward and reverse reactions.

(ii) Free-energy relationships in Co^{III} *substitutions*

This behaviour is exemplified by the aquation of dipositive acidopentaamminecobalt(III) complexes ($M = Co^{III}$, $L = NH_3$, $Y = H_2O$, various X^-) [4,7,66—68], for which an excellent LFER of slope 1.00 ± 0.03 exists for cases in which Co—X and $Co—OH_2$ bond-breaking is involved (cases such as X = arsenate, where bond-breaking occurs[69] between O and As rather than Co and O, must obviously be excluded). Alternatively, we may note that the anation rate coefficients for all X^- lie within a two-fold range, despite a 10^4-fold variation in aquation rates k_{CoX}. For dinegative leaving groups X^{2-}, a plot of slightly different intercept (corresponding to 10-fold higher k_{CoX} for a given equilibrium quotient) but the same unit slope seems to apply[68], the difference in intercept being attributable to the neglect of the ion-pairing pre-equilibrium. Ion pairing can be expected to be fairly constant for a given charge-type[70] but more significant for X^{2-} than X^-, although the influence of formal charge is sometimes much less than anticipated[38,71] and in fact the separation of the $Co(NH_3)_5X^+$ and $Co(NH_3)_5X^{2+}$ lines is not great.

Haim[68] treats the LFER's for aquations of $Co(NH_3)_5X^{(3-n)+}$ in terms of a formal equilibrium between transition states

$$[Co(NH_3)_5OH_2{}^{3+}]^* + X^{n-} \overset{Q^*}{\rightleftharpoons} [Co(NH_3)_5X^{(3-n)+}]^* + H_2O \tag{10}$$

and finds that Q^* is almost constant for a given n ($Q^* \simeq 0.3\ M^{-1}$ for $n = 1$, $\simeq 3.0\ M^{-1}$ for $n = 2$). The interpretation of this[68] is in accordance with the picture outlined above.

A closely similar LFER of $\alpha = 1.0$ exists[72] for the base hydrolyses of $Co(NH_3)_5X^{(3-n)+}$, except that in this case the dinegative anions X^{2-} such as sulphate correlate with the X^- *. There is now ample evidence[73—76] that base hydrolyses of Co^{III} ammine or amine complexes proceed via a deprotonated (conjugate base, cb) species which dissociates in a rate-determining D step to give a five-coordinate intermediate (common to a given series of complexes) that survives long enough by virtue of *cis* π-bonding by the amido group[77,78] to allow CoL_5 to lose all "memory" of X, to undergo extensive stereochemical change and to discriminate to some extent between various alternative replacement ligands Y. This D_{cb} mechanism involves the Brønsted acidities of CoL_5X as well as Q_{IP}; the effects of changing the formal charge of the complex on these two factors are likely to be roughly compensatory, and so a single LFER fortuitously covers all members of a series CoL_5X regardless of the size of the charge on X^{n-}.

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* This correlation was originally given[72] in terms of stability quotients based on $Co(NH_3)_5OH_2{}^{3+}$ rather than $Co(NH_3)_5OH^{2+}$, but clearly the ΔG^0 axis need only be rescaled by an amount corresponding to pK_a for $Co(NH_3)_5OH_2{}^{3+}$.

The above LFER's are seen to be consequences of I_d and D_{cb} mechanisms*, although it is conceivable that D mechanisms might lead to a breakdown of the LFER if the five-coordinate intermediate is very long-lived (cf. some electron transfer reactions which involve intermediates of marked stability)[82]. Alternatively, the involvement of an unusually long-lived intermediate ML_5 may result in an LFER of slope less than 1.0, as apparently happens in the rather special case of the aquations of *trans*-Co(*trans*[14]diene)X_2^+ complexes[83]. However, we have argued elsewhere[45] that, in general, I_d and D mechanisms will normally both lead to LFER's of unit slope.

Bifano and Linck[84] showed that a rough LFER exists between the rates of spontaneous and Hg^{2+}-induced aquations of $Co(en)_2LCl$ species of various charges and geometries. These authors state that the slope of this LFER is about 0.6, but a value of 0.8 ± 0.2 would be more representative of the data as a whole, and it seems inadvisable to read much significance into these values. The lack of any similar correlation between the rates of the Fe^{2+}- and the Hg^{2+}-catalyzed aquations[84] is not unexpected, since the former involves reduction of the Co^{III} centre.

(iii) Reaction products of D and I_d processes

The D/I_d distinction becomes clearer when the nature and stereochemistry of the reaction products are considered. In an I_d mechanism, the leaving group X^{n-} remains in the second c.s. while Y enters; thus, Y = solvent will be strongly favoured over an anionic Y^{m-} because of the electrostatic effect of X^{n-} (i.e. an ion *triplet* is improbable relative to an ion pair and Y^{m-} will generally not be retained in the second c.s.). Indeed, the *initial* product of spontaneous substitution reactions of aqueous $Co(NH_3)_5X^{(3-n)+}$ is evidently always $Co(NH_3)_5OH_2^{3+}$, even in the presence[85] of high $[Y^{n-}]$. The five-coordinate intermediate species are thus not simply CoL_5^{3+}, but rather $[\{CoL_5^{3+}\}X^{n-}.xH_2O]$, so that they *differ* from one another, and from $[\{CoL_5^{3+}\}xH_2O]$, according to the nature of X^{n-}.

If, however, X *cannot* be retained in the second c.s., the intermediate will be $[\{CoL_5^{3+}\}.xH_2O]$, and will be the *same* for all reactions of this type. Cases in point are the "induced" aquations, for example, of halo complexes by Hg^{2+} and of azido complexes of NO^+, in which the leaving groups are HgX^+ and (N_2 + N_2O) respectively and obviously differ from anionic leaving groups in being unable to form ion pairs with the residual cationic five-coordinate complex. Thus it comes about that, for induced aquations within several series of Co^{III} complexes, stereochemical and competition experiments clearly show the presence of common intermediates which are *not* the same

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* An associative attack by H_2O may occur[79,80] in the aquation of *trans*-Co(trien)Cl_2^+ (but see ref. 2, p. 261), and a complicated associative mechanism has been suggested for the replacement of Cl^- by 1,2-cyclohexanedione in aqueous *trans*-Co(en)$_2Cl_2^+$, which proceeds faster than Cl^- aquation[81].

as those encountered in the analogous spontaneous aquations[80,86—89]. Indeed, the mere fact that anionic Y^{n-} can compete significantly for the CoL_5^{3+} generated in induced aquation arises because the departing group is not a dipolar neutral ligand or an anion and so is immediately lost from the second c.s.; the intermediate is nonetheless short-lived, and therefore shows little discrimination between alternative Y^- other than a slight preference for those which require the least desolvation ($NO_3^- > Cl^- \simeq Br^- > F^-$)[90].

For the D_{cb} mechanism, the existence of a common five-coordinate amidocobalt(III) complex throughout a given series of base hydrolyses is again reflected in the results of competition[91] and stereochemical[78,92,93] experiments. The lifetime of $Co(NH_3)_4NH_2^{2+}$ generated in such experiments is evidently of the order of the timescale of diffusion-controlled processes[90], but it is at least long enough to permit the complete separation of X^{n-} from the second c.s.

(iv) Associative mechanisms

While the existence of linear Brønsted plots of slope 1.0 is expected for I_d or D mechanisms involving short-lived intermediates, it is not immediately obvious whether smooth Brønsted plots should exist at all for associative mechanisms, or, if they do, whether α should be constant[94]. Edwards was the first inorganic chemist to consider this problem, and the reader is referred to Chapters 3 and 4 of his book[5] for applications of free energy relationships to the associative substitution reactions occurring at square-planar Pt^{II} centres; however, it was not evident in 1964 whether the consequences of associative substitution at octahedral centres should be considered.

Following Leffler and Grunwald[65], we may suppose that ΔG^{*}_{MX} is a linear combination of the free energies of reactants and products, and present eq. (6) in terms of small increments δ.

$$\delta G^{*} = b\,\delta G_{MX} - (1-c)\delta G_{MY} \tag{11}$$

If we assume that M—X bond-breaking occurs only synchronously with M—Y bond-making (i.e. that we have an I_a mechanism), then changes in G_{MX} will be geared to changes in G_{MY}*, so that

$$\delta G^{*} = \alpha\,\delta G_{MY} + (1-\alpha)\delta G_{MX} \tag{12}$$

where α is an approximate measure of the fractional displacement of the transition state along the reaction coordinate from reactants to products.

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* Leffler and Grunwald[65] justify the development of eqn. (12) from eqn. (11) on the grounds that it is reasonable to assume that changes in δG^{*} will be intermediate to the corresponding changes for the reactants and the products; in fact, the parameters b and c of eqn. (11) can be replaced by the single parameter α only if there is a physical link between bond-making and bond-breaking, or if α, b and c are 1.0.

From eqn. (12), the Brønsted relation follows

$$\delta \Delta G^{*} = \alpha\, \delta \Delta G^{\circ} \tag{13}$$

The transition state will bear more resemblance to the reactants than the products, and α will be considerably *less* than 0.5, if ΔG° is strongly negative; conversely, if ΔG° is strongly positive, α will be between 0.5 and 1.0, and the transition state will be essentially product-like. In the case of the I_d substitutions discussed above, the "products" are solvated $\{ML_5 + X + Y\}$, as far as the rate-determining reaction profile is concerned, so that $\alpha = 1.0$. For *slow* I_a substitutions, ΔG^{*}_{MX} is large (~ 25 kcal.mol^{-1} in typical cases) relative to ΔG° (~ 0 ± 5 kcal.mol^{-1}), so that α should be close to 0.5 and will likely appear constant within the experimental uncertainty, even though the Brønsted plot should be curved if a large enough range of ΔG° can be covered. In other words, slow I_a substitutions are expected to give rise to LFER's of slope $\alpha \simeq 0.5$.

Atom (especially proton) and electron transfer reaction rates often yield non-linear Brønsted plots, and can be seen to be crudely analogous to I_a substitution in $ML_5X + Y$ if this reaction is viewed as the transfer of an ML_5 entity (common within a series of ML_5X) from X to Y. For proton transfers, Bell[95,96] showed that the Brønsted equation (13) ($1 > \alpha > 0$) should hold for (e.g.) the protonation of a common base by a series of related acids if the Morse curves of the acids were parallel and not too widely separated, and further that $\alpha = \frac{1}{2}$ if the slopes of the Morse curves were equal (but of opposite sign) to that of the Morse curve of the protonated base at the point of intersection. Marcus[97] has shown theoretically that, for atom transfer between relatively large weakly interacting polyatomic molecules, smooth Brønsted relationships should exist with the local Brønsted slope being

$$\alpha = \tfrac{1}{2}\,[1 + (\Delta G^{\circ}/4\Delta G^{*}_{0})] \tag{14}$$

where ΔG^{*}_{0} is the value of ΔG^{*} corresponding to $\Delta G^{\circ} = 0$, and $\Delta G^{\circ} < 4\Delta G^{*}_{0}$. In fact, smooth Brønsted plots with curvatures of the magnitudes predicted by eqn. (14) have been shown by Marcus[97] and most recently Kreevoy and Oh[98] to fit the experimental data for several series of proton transfer reactions, in which ΔG^{*}_{0} is not large relative to ΔG°.

Kreevoy and Oh's analysis also shows that most of the heavy-atom and solvent reorganization that accompanies proton transfer precedes or follows the rate-determining step. When defining the I mechanisms of octahedral substitution (Section B), we suggested that this also applies to solvent reorganization in these systems in which the five- or seven-coordinate intermediates are not long-lived on the timescale of relaxation of the second c.s.

From eq. (14), we see that α is about $\frac{1}{2}$ for atom-transfer reactions if ΔG^{*}_{0} is much greater than $|\Delta G^{\circ}|$. The latter condition holds for slow I_a substitutions of ML_5X, to which the Marcus theory was not intended to apply but which may show some similarities to atom-transfer, as noted above.

To date, only German, Dogonadze and co-workers[99—105] have published a detailed theoretical approach to the question of the systematics of the kinetics of octahedral aquation reactions. They assume that the potential energies of the initial and final complexes, ML_5X and ML_5OH_2, are parabolic functions of the displacements along the reaction coordinate away from the ground-state configuration. This leads to eqn. (15) for the activation energy E_a (this could be recast in terms of free energies, for the purposes of this section)

$$E_a = E_r^{aq} + [E_s + \Delta E + E_r^x - E_r^{aq}]^2/4E_s \qquad (15)$$

where E_r^x, E_r^{aq} and E_s are the reorganizational energies of X, water and ML_5X, and ΔE is the internal energy change for the reaction on going to equilibrium. If E_r^x, E_r^{aq} and E_s could be taken to be roughly independent of ΔE for a series of reactions, E_a would correlate with a *quadratic* function of ΔE, and the local slope α_E of a plot of E_a vs. ΔE (or the Brønsted slope, if eqn. (15) is written in terms of free energies) would be given by

$$\alpha_E = \tfrac{1}{2} + [(\Delta E + E_r^x - E_r^{aq})/2E_s] \qquad (16)$$

German and Dogonadze[100] calculate that when ML_5 is $Cr(OH_2)_5^{3+}$, E_{aq} (which is constant) $\simeq 21$, $E_r^x \simeq 5$, and $E_s = 40$ (X = I), 47 (Cl) and 65 (F) kcal.mol^{-1}, while ΔH^0 ($\simeq \Delta E$) is known to range between +2 and −8 kcal.mol^{-1} for a variety of typical X^-. Thus, in practice, the difference $(\Delta E + E_r^x - E_r^{aq})$ is markedly less than $2E_s$, so that α_E and α will be roughly constant and near 0.5. In other words, the term in ΔE^2 in the quadratic relating ΔE and E_a is unimportant relative to that in ΔE, so that once again I_a substitution processes are predicted to lead to an approximate LFER of slope about 0.5.

However, it is unlikely that ΔE is independent of E_r^x and E_s, though changes in these parameters throughout a reaction series may be largely self-compensatory. Furthermore, the assumption of a *parabolic* shape for the Morse curve over the region of interest seems unrealistic, since we are concerned with the stretching of the M—X bond to destruction, rather than the small vibrational displacements for which the parabolic relationship suffices. This point is illustrated in Fig. 2, which is Fig. 1 redrawn so that the pseudo-Morse curve for ML_5—X bond stretching intersects that for ML_5—Y, which means that Y—M bond formation is under way before M—X fission is complete (an I_a criterion).

Figure 2 corresponds to a combination of German—Dogonadze energy profiles for ML_5X, ML_5Y, free X and free Y, recast in terms of free energy and referred to the common reference free energy of $\{ML_5 + X + Y\}$, appropriately solvated (as in Fig. 1). The algebraic sum of these gives the free-energy profile (G^*) for an I_a mechanism, which will therefore have a maximum at $G^* = \Delta G^*_{MX}$ when the slope of G^* is zero, i.e. when the pseudo-Morse curves have equal slopes of opposite sign. Since, for comparably large values of G_{MX} and G_{MY}, the pseudo-Morse curves for ML_5X and ML_5Y will not be very

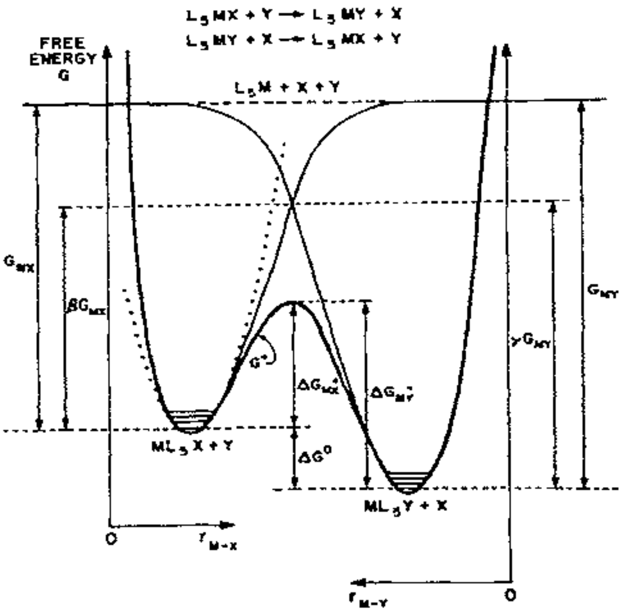


Fig. 2. Free-energy profile for an I_a mechanism.

different in size of shape, this condition will obtain at some point along the reaction coordinate very close to the intersection point of the Morse curves, although strictly speaking ΔG^*_{MX} will be placed at the actual Morse intersection point only if X = Y, as in an aquo-exchange reaction. The G^* curve will also be rather flat in this region, as Fig. 2 illustrates.

As Fig. 2 is drawn, the transition state is reached at a point on the reaction coordinate where the M—X bond is 70% broken in terms of free energy (i.e. $\beta = 0.70$) while the M—Y bond is only 25% formed ($\gamma = 0.75$), yet ΔG^*_{MX} is lowered to only 40% of the value (G_{MX}) it would have in an I_d process. In an extreme case, ΔG^* for a symmetrical I_a reaction would be zero if the bonds were just 50% broken/formed in the transition state. The point here is that the transition state in I_a corresponds to M—X bond stretching far beyond the region where the approximate parabolic law (dotted curve in Fig. 2) applies. The exact functional forms of the pseudo Morse curves of Fig. 2 are not known, but in the region of intersection the dependence G_{MX} on r_{M-X} and G_{MY} on r_{M-Y} is obviously of lower order than parabolic. If a local linear dependence is assumed (and Fig. 2 has been drawn to show that this is reasonable), then E_a becomes a linear, rather than a quadratic, function of ΔE in the German—Dogonadze treatment[105], and by the same token the Brønsted plot becomes linear.

Rewriting eqn. (6) for the transition state

$$\Delta G^*_{MX} = \beta G_{MX} - (1 - \gamma) G_{MY} \tag{17}$$

and, noting that if the transition state occurs approximately where the pseudo-Morse curves intersect we can write

$$(1-\beta)G_{\mathrm{MX}} \simeq (1-\gamma)G_{\mathrm{MY}} \tag{18}$$

(see Fig. 2), we have

$$\Delta G^{*}_{\mathrm{MX}} \simeq (2\beta - 1)\,[\Delta G^{0} + G_{\mathrm{MY}}] \tag{19}$$

or alternatively

$$\Delta G^{*}_{\mathrm{MX}} \simeq \Delta G^{0} + (2\gamma - 1)G_{\mathrm{MY}} \tag{20}$$

since, with reference to the $[\mathrm{ML_5X} + \mathrm{Y}]$ baseline,

$$\Delta G^{0} = |G_{\mathrm{MX}}| - |G_{\mathrm{MY}}| \tag{21}$$

For a series of reactions with the same Y, M and L, G_{MY} is constant, and according to eqn. (20), γ must either be 1.00 or else vary with ΔG^0 (and hence with G_{MX}); similarly, from eqn. (19), the existence of an LFER would require that β be the same for all X within the series. Thus, the existence of an LFER of slope less than 1.0 implies that the degree of M—Y bond formation called into play is controlled by the nature of the bond to be broken, while the extent of bond-breaking is constant within a series of fixed M, L and Y and is characteristic of the attacking nucleophile Y.

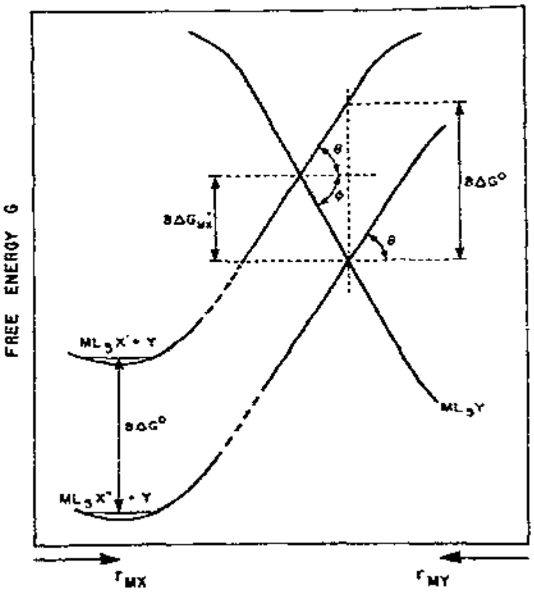


Fig. 3. Detail of an $\mathrm{I_a}$ free-energy profile for the formation of a common product $\mathrm{ML_5Y}$ from a series of reactants $\mathrm{ML_5X'}$, $\mathrm{ML_5X''}$, etc.

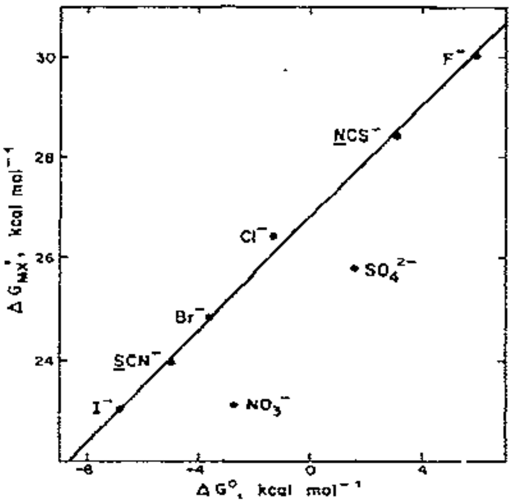


Fig. 4. Relationship between the free energy of activation ΔG^*_{MX} and the free energy of reaction ΔG^0 for the acid-independent aquation of $(H_2O)_5CrX^{(3-n)+}$ (25°C, ionic strength 1.0 *M*, perchlorate media). Data from refs. 46, 51, 52 and 106.

Finally, the highly stylized Fig. 3 illustrates Bell's argument[96], that the slope of Brønsted plot will be 0.5 if the slopes θ of the parallel Morse curves of reactants ML_5X', ML_5X'', etc., are equal but opposite to the slope ϕ of the Morse curve of the common reaction product ML_5Y at the point of intersection, assuming that the Morse curves can be approximated locally to straight lines. These conditions are likely to be approximately true for typical series of complexes, the complete Morse curves of which will be very similar in size and shape, and it follows from the trigonometry of Fig. 3 that

$$\alpha = (\delta \Delta G^*_{MX} / \delta \Delta G^0) = 0.5 \tag{22}$$

if $\theta = \phi$ numerically and δ represents *small* increments.

(v) Free-energy relationships in Cr^{III} *substitutions*

In summary, then, an I_a mechanism can normally be expected to produce an LFER of slope near 0.5. This behaviour is found[52] for the aquation of $(H_2O)_5CrX^{(3-n)+}$, as in Fig. 4. The slope α is 0.56 (at 25°C, $I = 1.0$ *M*), so that the degree of Cr—X bond-breaking β is typically 78% for $X^- = F^-$, Cl^-, Br^-, I^-, $\underline{N}CS^-$ and $\underline{S}CN^-$. In simpler terms, this means that the rate of substitution of H_2O in $Cr(OH_2)_6^{3+}$ by these X^- is markedly dependent on the nature of X^-; thus, the rate of attack of $\underline{N}CS^-$ is 2×10^3 times faster than that of I^- (25°C, $I = 1.0$ *M*)[94], in sharp contrast to the very narrow range of anation rates for $Co(NH_3)_5OH_2^{3+}$ (Section D(ii)).

The failure of $(H_2O)_5CrOSO_3^+$ to correlate with $(H_2O)_5CrX^{2+}$ is scarcely surprising, by analogy with the charge-type dependence of the LFER for aquations of $(NH_3)_5CoX^{(3-n)+}$, but the deviation of the supposedly monodentate nitrato complex suggests some mechanistic anomaly, especially since $Co(NH_3)_5NO_3^{2+}$ fits the Langford LFER[66]. This is apparently not due to O—N as opposed to Cr—O bond-breaking[94], but is probably related to the strong *cis*-activating properties of NO_3^- bound to Cr^{III}, established[43] for $Cr(NH_3)_5NO_3^{2+}$ and presumably operative in "$Cr(H_2O)_5NO_3^{2+}$" since the apparent aquo-exchange rate of $Cr(H_2O)_6^{3+}$ is markedly higher in aqueous nitrate than in aqueous perchlorate media[107]. The *cis*-activating property of NO_3^- is probably due to associative ring-closure resulting in a transiently bidentate nitrato ligand[43] (an appealing hypothesis, since it will be associated specifically with I_a-prone systems); it may well be that "$(H_2O)_5CrONO_2^{2+}$" is in fact predominantly bidentate in solution, with an anomalously high stability constant (excessively positive ΔG^0 in Fig. 4) accordingly, but a careful search for a relatively rapid initial ring-opening step in its aquation was fruitless[108]. The formation and aquation of $(H_2O)_5CrOSO_2^+$ and $(H_2O)_5CrONO^{2+}$ evidently *do* proceed without Cr—O bond fission[109,110], and so these are not expected to fit the LFER.

Thusius[111], following Haim[68], has pointed out that Q^* for the hypothetical equilibrium

$$[(H_2O)_5Cr(OH_2, X)]^* \rightleftharpoons [(H_2O)_5Cr(X,OH_2)]^* \tag{23}$$

varies widely with X, as expected for an I_a mechanism and in sharp contrast with the narrow range of Q^* values found[68] for the I_d anations of $Co(NH_3)_5OH_2^{3+}$.

ΔG^*_{CrX} values for the aquation of $Cr(NH_3)_5X^{2+}$ at 25°C plot essentially linearly against those for $Cr(OH_2)_5X^{2+}$ (X = F, Cl, Br, I, NO_3, NCS)[43,45,112–114] with a slope of 0.9, which suggests that the Brønsted plot for the $Cr(NH_3)_5X^{2+}$ series should also be essentially linear. However, ΔG^0 data are presently lacking for the ammine series except for X = Cl and NCS (ref. 44).

While the acid-independent aquation pathways of $(H_2O)_5CrX^{2+}$ (rate coefficient k_0 in eqn. (2)) yield an LFER of slope 0.56, the corresponding plot for the term with inverse $[H^+]$ dependence (k_{-1} in eqn. (2)) is roughly linear[94] with $0.9 < \alpha \leq 1.0$. The spread in rate coefficients for the *reverse* of this pathway is small (about 17-fold for the reactions studied so far, or less than 1% of the range in anation rates for $Cr(OH_2)_6^{3+}$) and is probably due solely to differences in the pK_a values of the various $Cr(OH_2)_5X^{2+}$. Thus, the k_{-1} pathway is probably a D_{cb} process as opposed to I_a for k_0, and this difference in mechanism can explain the decline in importance of k_{-1} relative to k_0 as X ascends the spectrochemical series, since D mechanisms may be expected to be more sensitive than I_a toward ligand-field effects[94].

The semi-quantitative correlation of the ligand-field splitting with k_0/k_{-1} predicts a value of ~ 100 M^{-1} for this ratio for the $Cr(H_2O)_6^{3+}$ aquo-exchange[94] at 25°C, $I = 1.0$ M; preliminary experiments[115] indicate $k_0/k_{-1} = (8.3 \times 10^{-5})/(1.2 \times 10^{-6}) = 70$ M^{-1} (at 50°C, $I = 0.7$ assuming that all six aquo ligands exchange. (A similar ratio evidently applies to the $Fe(OH_2)_6{}^{3+}$ aquo exchange[116].) Taking pK_a to be 3.64 for $Cr(OH_2)_6{}^{3+}$ at 50°C and $I = 0.5$ (ref. 117), we can estimate $k_{ex} = 5 \times 10^{-3}$ sec^{-1} for the exchange of all six waters in $Cr(OH_2)_5OH^{2+}$, or over 60 times k_{ex} for $Cr(OH_2)_6^{3+}$ under these conditions[47]. By way of comparison, if $pK_a = 5.1$ and $k_{-1} = 2.8 \times 10^{-8}$ M.sec^{-1} for $(H_2O)_5CrCl^{2+}$ at 25°C (refs. 42, 118), $(H_2O)_4Cr(OH)Cl^+$ aquates with $k_0 = 3.6 \times 10^{-3}$ sec^{-1}, or 1.3×10^4-fold faster than $(H_2O)_5CrCl^{2+}$. Thus, the claim[119] that the porphyrin system in $Cr(TPPS)OH(OH_2)^0$ labilizes the Cr complex toward substitution 10^3- to 10^4-fold relative to "normal" Cr complexes is invalid, since the effect can be ascribed wholly to the presence of the OH^- ligand.

For the spontaneous aquation of $(H_2O)_5CrX^{(3-n)+}$, where X^{n-} has appreciable Brønsted basicity (pK_a of $HX \geqslant 2$), a pathway first-order in $[H^+]$ is observed (coefficient k_1 in eqn. (2)) in which the separating entity is evidently $HX^{(n-1)-}$. In such cases, the corresponding k_0 path exhibits anomalously large ΔH_0^* and ΔS_0^* values (see Sections E and F) and this has been attributed[13] to the separation of $HX^{(n-1)-}$ from $CrOH^{2+}(aq)$, rather than X^{n-} from $Cr^{3+}(aq)$, in the transition state (see also Seewald and Sutin[116]).

This idea has recently received support from Asher and Deutsch's observation[120] that ΔG^* values for the k_1 and k_0 paths for $X^- = CN^-$, CH_3COO^-, N_3^- and F^- are related by one straight line of unit slope, and $^-SC_6H_4NH_3{}^+$ and $^-SCH_2CH_2NH_3{}^+$ by another. Fluoropentaaquochromium(III) nevertheless correlates well with $(H_2O)_5CrX^{2+}$ derived from "non-basic" X^- in Fig. 4 because the major difference between the $HX/CrOH^{2+}$ and the X^-/Cr^{3+} mechanisms is one of solvation in the transition state. If solvation changes are likened to freezing or thawing of solvent, for which ΔG^0 is small by chemical standards for most solvents over their normal liquid ranges, it can readily be seen that ΔG^* should indeed be relatively insensitive to solvational differences, although these may produce large but compensatory anomalies in ΔH^* and $T\Delta S^*$ (Sections E and F)[8,52,121].

If X in $Cr(OH_2)_5X^{2+}$ can be converted to a "good leaving group" which has a negligible residence time in the second c.s., one would expect an LFER of slope close to 1.0, since the mechanism will be essentially D. Birk and Ingerman[122] observed an LFER of $\alpha = 0.90 \pm 0.02$ for the Hg^{II}-catalyzed aquation of the halopentaaquochromium(III) ions (leaving group HgX^+), in accordance with this prediction, although the shortfall in α from 1.00 could be attributed to a slight I_a bond-making tendency by the incoming water molecule in the transition state (γ and β both near 1.0). The Hg^{II}-catalyzed aquation of the thiocyanato-N analogue does not fit this correlation, presumably because (a) it involves a well-defined pre-equilibrium step, and (b) Hg^{2+} can be expected to attach itself to the S atom in NCS, and not the N end (which is the reaction site).

(vi) Reaction products of I_a substitutions

If, in an I_a mechanism, a nucleophile Y can compete with the solvent in direct attack on ML_5X with the displacement of X, we can expect the fractional yield of ML_5Y to depend significantly upon the nature of X, whereas in a D process the ML_5 intermediate has lost all memory of X when Y enters the first c.s. (the I_d case will tend to yield the solvento-complex to the exclusion of ML_5Y, as explained in Section D(iii)). Ardon[123] found that the disappearance of $(H_2O)_5CrI^{2+}$ in 1.0 *M* HY (Y = Cl or Br) proceeded at about the same rate as in 1.0 *M* $HClO_4$, but gave yields of $(H_2O)_5CrY^{2+}$ (relative to $(H_2O)_6Cr^{3+}$) far in excess of the equilibrium values. This was taken to indicate a D mechanism.

However, medium effects could easily swamp the small accelerations of the rate of disappearance of $(H_2O)_5CrX^{2+}$ anticipated for concurrent I_a attacks by H_2O and Y (although a subsequent study[94] of the aquations of several $(H_2O)_5CrX^{2+}$ in 1.0 *M* $HClO_4$ and HCl showed that small accelerations due to Cl^- *do* occur). Furthermore, in the "induced" aquation of $(H_2O)_5CrN_3^{2+}$ by NO^+ (which is the reaction most likely to generate $(H_2O)_5Cr^{3+}$)[124,125], there is far less incorporation of Cl^- or Br^- than reported[123] for the spontaneous aquation of $(H_2O)_5CrI^{2+}$ under similar conditions, the intermediate (if it exists) being highly reactive and of low ability to discriminate between Cl^- and Br^-. Finally, when $(H_2O)_5CrX^{2+}$ (X = Br, I, NO_3, and $\underline{S}CN$) are aquated in 1.0 *M* HCl, the relative yields of $(H_2O)_5CrCl^{2+}$, corrected for its own aquation and for the contribution of the conjugate-base pathways to the yield of $(H_2O)_6Cr^{3+}$, depended markedly on the nature of X (35, 19, 19 and 6% respectively)[94].

These results indicate that Y^- incorporation following spontaneous aquation does not occur through scavenging by a common $Cr(OH_2)_5{}^{3+}$ intermediate. Nor, however, does our earlier interpretation[94] involving competitive I_a attacks by Y^- and H_2O now seem satisfactory, since, as remarked in Section C(iv), relatively "soft" species such as Cl^- and Br^- are unlikely to be able to compete effectively with "hard" H_2O (which is in large excess in any case) for the "hard" Cr^{III} centre. The incorporation of Y^- is probably the consequence of the activation of one or more of the five H_2O ligands in $(H_2O)_5CrX^{2+}$ by X toward substitution, as suggested by Moore et al.[126]; thus, one aquo ligand (presumed *trans*) in $(H_2O)_5CrI^{2+}$ exchanges with solvent 3.3 times faster than I^- is lost[42,126], so that a significant fraction of the iodo complex could conceivably aquate to $(H_2O)_5CrCl^{2+}$ via the formation of the presumably relatively labile intermediate $(H_2O)_4CrICl^+$.

Our original interpretation[94] of the Cl^- incorporation data favoured effective I_a attack by Cl^- rather than the mechanism given by Moore et al. because the order of the corrected relative yields of $Cr(OH_2)_5Cl^{2+}$ (X = Br > I = NO_3 > $\underline{S}CN$) seemed inconsistent with any general theory or observations concerning relative *trans*-activating powers, which are expected to be I > Br $\simeq$ $\underline{S}CN$ $\gg$ NO_3. However, recent investigations by Baldwin and Keen[127,128] have shown that one H_2O in $(H_2O)_5CrBr^{2+}$ exchanges 14 times faster than Br^- is lost, so that $(H_2O)_5CrBr^{2+}$ would be considerably more vulnerable to Cl^- incorporation by the mechanism of Moore et al. than would $(H_2O)_5CrI^{2+}$, despite the fact that the actual rate of exchange of the singular H_2O in the latter is 5 times faster than in the bromo complex (i.e., the *trans*-effect of I^- *is* greater than that of Br^-, but the bromo complex survives long enough to incorporate more Cl^-). Furthermore, the nitrato ligand has been found to be a powerful *cis*-activator in Cr^{III} complexes[43], and its expected low status as a *trans*-activator[94] is therefore irrelevant to the question of Cl^- incorporation. The *trans*-activating property of I^- in Cr^{III} systems has in the meantime received independent verification[23,24,129,130].

The theory of the *trans*-effect[131] leads to the expectation that it will be especially important in complexes with class "b" characteristics[34], e.g. in $(H_2O)_5RhCl^{2+}$, where the aquo group *trans* to Cl is strongly activated toward substitution by a D mechanism[30]. This mechanism may be expected to operate at *trans*-activated sites in octahedral complexes, in which the *trans*-influence is believed to be transmitted by a σ-type electronic interaction, and indeed this seems to be the case for *trans*-activated substitution even when the "normal" substitution mechanism[29,30,127,128,132] is I_a.

While ligands such as iodo[24,126,129,130] and sulphito-S (ref. 132) seem to be exclusively *trans*-activators, this is not true for hydroxo in conjugate-base substitutions of Cr^{III} complexes[109], and Nordmeyer[78] has shown that the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ proceeds via *cis*-$Co(NH_3)_4(NH_2)X^{(2-n)+}$. However, in all these cases the reaction characteristics are consistent with D or D_{cb} mechanisms. On the other hand, the striking effectiveness of NO_3^-, SO_4^{2-} and other oxyanions in labilizing ligands *cis* to them in Cr^{III} complexes is not easily attributable to electronic effects, since other class "a" ligands such as F^- or OH^-, which should have electronic properties similar to the oxyanions, are much poorer *cis*-activators[43]. The obvious common property of the oxyanions is their potential for chelation, and this, combined with the evident capacity of Cr^{III} for I_a substitution, provides a reasonable explanation for their *cis*-activating power[43].

Ferraris and King[23] showed that the spontaneous solvolysis of $(H_2O)_5CrI^{2+}$ (extrapolated to zero time, i.e. to the exclusion of aquo/solvent exchange) and the "induced" solvolyses of azido- and halopentaaquochromium(III) ions in aqueous methanol all lead to about the same relative amounts of $(H_2O)_6Cr^{3+}$ and $(H_2O)_5Cr(MeOH)^{3+}$. These results suggest (but, as Ferraris and King[23] point out, do not *prove*) that these three reactions proceed by a common mechanism, presumably of the D type. However, this observation does not necessarily invalidate our general thesis that I_a mechanisms prevail in substitutions at Cr^{III} centres in the absence of special factors such as *trans*-activation or deprotonation, because the "hard" Cr^{III} centre will not discriminate *electronically* to a significant extent between the "hard" nucleophiles H—OH and Me—OH, both of which would present O atoms in similar environments to the Cr^{III} centre in I_a attacks[45]. Discrimination should be especially small for "good leaving groups" such as I^-, for which γ (eqn. (21) and Fig. 2) would be near 1.0.

Baltisberger and Hanson[133], on the other hand, conclude from their study of the catalysis by methanol of the anation of aqueous $(H_2O)_6Cr^{3+}$ by NCS^- that a D mechanism is *not* operative in this reaction. This is in accordance with Baltisberger and King's[17] earlier tentative conclusion, drawn from studies of the $Cr^{III}—Cl^-$ system in aqueous methanol, that exchange of H_2O between $(H_2O)_6Cr^{3+}$ and bulk solvent does *not* involve a D process. In summary, then, we can say that the products and kinetics of Cr^{III} substitution reactions can be rationalized on the basis of a general I_a mechanism, except where a powerful *trans*-activator is present or a conjugate base pathway is involved, in which cases a D or D_{cb} process may take effect.

(vii) Stereochemical consequences of mechanistic type

The stereochemistry of octahedral substitution has been reviewed at length elsewhere[1,2,134]. With regard to the systems considered above, it can be said generally that I_a processes are stereoretentive; those reactions which involve steric change are I_d or D (and especially D_{cb}, wherein π-stabilization is thought to favour rearrangement of square-pyramidal ML_5 moieties to trigonal-bipyramidal).

A stereoretentive I_a process must proceed[135] by a "flanking" or "*cis*" attack by Y, relative to X, on M in ML_5X. If steric change is to occur at all in an I_a process, it must do so by "remote" or "*trans*" attack of Y relative to X, and a ligand L must be displaced *without* M—L *bond fission* to take the place of the departing Y. This is unlikely to occur, since if L can be displaced in this way it is well on the way to being expelled itself. Furthermore, facilitation by X of *trans* attack evidently leads to dissociative loss of *trans*-L, and not to associative attachment of Y without loss of L.

Vanderheiden and King[24] report a case in which it appears that an acid-independent solvolysis pathway for a Cr^{III} complex might proceed with *some* steric change. Loss of iodide from *trans*-$(H_2O)_4Cr(DMSO)I^{2+}$ in aqueous DMSO (0.705 mole fraction DMSO) leads to both *cis*- and *trans*-$(H_2O)_4Cr(DMSO)_2^{3+}$, as well as $(H_2O)_5Cr(DMSO)^{3+}$; the observed *cis/trans* ratios for 25°C and $I = 0.53$ M were 0.27 and 0.82 for $[H^+] = 0.52$ and 0.04 M, and increased (at the lower acidity) with decreasing $[H^+]$. These results, taken on their own, indicate that the conjugate-base solvolysis pathway involving $(H_2O)_3(HO)Cr(DMSO)I^+$ is a more important source of the *cis*-bis(DMSO) product than the acid-independent path, but the possibility remains that the latter route leads to some *cis* product.

If the $[H^+]$-independent path were typically I_a and gave no *cis* product, and if the conjugate-base path gave no *trans*, the rate data of Table IV or ref. 24 predict that the *cis/trans* ratio would be 0.15 and 2.0 at $[H^+] = 0.52$ and 0.04 M respectively. These figures must be corrected for the products of the reaction of $(H_2O)_5Cr(DMSO)^{3+}$ with DMSO, which unfortunately has not been examined under the appropriate experimental conditions but which should statistically give a *cis/trans* ratio of 4, i.e. its effect should be to increase the *cis/trans* ratio for the solvolysis reaction. This is likely to be more important at high [H$^+$] than at low, relative to iodide loss[94]. Thus, the experimental data are not necessarily inconsistent with a purely stereoretentive [H$^+$]-independent pathway in the solvolysis of *trans*-$(H_2O)_4Cr(DMSO)I^{2+}$ (as expected for I_a), but require that the pathway involving $(H_2O)_3(HO)Cr(DMSO)I^+$ give both *cis*- and *trans*-$(H_2O)_4Cr(DMSO)_2^{3+}$, as seems likely for a D_{cb} process (some 30—40% *trans* in this pathway would be reasonable).

The absence of detectable steric change in the spontaneous or induced aquations and base hydrolyses of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)X^{2+}$ (X = Cl, Br, I)[136—138] serve to emphasize that, while it can be argued that stereochemical rearrangements in octahedral substitution are invariably associated with D or I_d modes of reaction, the converse is far from true. The experimental evidence presently available indicates that stereochemical change is common for Co^{III} reactions, in which D_{cb} processes are especially effective and simple substitution is I_d or D, but rare for Cr^{III} and Rh^{III}, for which I_a is evidently prevalent and D_{cb} processes are not so strikingly efficient.

The effect of sufficiently bulky ligands L should be to accelerate I_d processes and retard I_a markedly. Foxman[139] has shown that even the replacement of L = NH_3 by L = CH_3NH_2 in L_5CoCl^{2+} is enough to cause marked distortions of the ground state of the complex by steric compression, and the impressive accelerations of chloride aquation (× 22) and base hydrolysis ($\times 1.5 \times 10^4$) at 25°C associated with this change of L clearly reflect the prevalence of I_d and D_{cb} mechanisms at Co^{III} centres[140]. The steric decompression effect is greater for base hydrolysis than for aquation because the former proceeds with steric change, whereas aquation is stereoretentive[93,141]; that is, the rearrangement of the five-coordinate conjugate-base intermediate from tetragonal-pyramidal to trigonal-bipyramidal to permit π-stabilization by the amido ligand results in a large relaxation of steric compressions, whereas the relatively small movements of the four *cis* NH_3 groups away from the *trans* in forming the C_{4v} I_d intermediate will be less effective in relieving congestion.

For the analogous $(RNH_2)_5CrCl^{2+}$ aquations[142], a 33-fold retardation occurs when R = H is replaced by R = CH_3, as expected for an I_a process. The compressional effect of adding a seventh ligand Y (as in I_a) should be much more dramatic than the decompressional effect of taking the sixth ligand X away (as in I_d); the effect is indeed somewhat greater for the Cr^{III} series than for the Co^{III}, and would presumably be much more so were it not for the fact[143,144] that the ionic radius of the central Cr^{3+} ion is about 17% larger than that of low-spin Co^{3+}. By the same token, if the base hydrolysis of $(RNH_2)_5CrCl^{2+}$ is D_{cb}, as expected, then the increase in rate from R = H to R = CH_3 should be large but less than for the Co^{III} analogues; indeed, the increase is 225-fold at 25°C (ref. 142).

Progress from R = CH_3 to R = CH_3CH_2 and other *n*-alkyl groups will not change the steric congestion at the reaction site significantly, but will lead (in aqueous solution) to progressive desolvation of the ground states *and* transition states as the ligands become ever more "water-repellent". The exact implications of this are not obvious, but the *direction* of the effect on hydrolysis rates should be the same whether the mechanism be I_a, I_d or D_{cb}. Indeed, a general, relatively slight increase in the rates of spontaneous aquation and base hydrolysis of $(RNH_2)_5MCl^{2+}$ occurs as R changes from CH_3 to CH_3CH_2 and so forth, whether M = Co (ref. 140) or Cr (ref. 142). This effect resides in ΔH^* and ΔS^* rather than ΔG^*, for M = Cr at least[142], and this is as expected for solvational effects[8,52,121].

(viii) ΔG^* relationships for solvents other than water

The solvolysis of $(NH_3)_5CoCl^{2+}$ in aqueous ethanol yields an LFER between ΔG^*_{CoCl} and ΔG^0 as the solvent composition is varied[145]. The slope is 0.35 at 40°C and 0.44 at 30°C. Water was in at least a threefold molar excess over ethanol in these experiments, and, since no $(NH_3)_5Co(EtOH)^{3+}$ was detected, the reaction was essentially the same in all of them. The LFER probably represents changes in the ion-pair formation quotient and/or changes in the ethanol content of the second c.s. as the ethanol content of the bulk solvent is varied.

Values of log *k* for the aquations of $Co(NH_3)_5Cl^{2+}$ and *trans*-$Co(en)_2Cl_2^+$ in a variety of aqueous—organic mixed solvents are linear functions of the Grunwald—Winstein *Y* parameters for these solvents, with slopes near 0.3 in all cases[146]; the analogous bromides give slopes[147] near 0.2. Thus, variation of solvent composition has a surprisingly small effect on these aquation rates, by comparison with those of S_N1 organic solvolyses, and preferential solvation of the complex cations by water is probably responsible for this. However, the extensive studies by King and co-workers[17—24,148] emphasize that substantial amounts of organic solvents (especially methanol) *can* be present in the first and second coordination spheres of the solvated Cr^{3+} ion in aqueous—organic solvents.

Langford[149] has pointed out that the rates of solvolysis of *trans*-$Co(en)_2Cl_2^+$ differ only by a factor of about three in methanol and *N,N*-dimethylformamide (DMF), whereas the activity of Cl^- would change by a factor of about 10^6 on being transferred from methanol to DMF. This appears to run counter to the conventional wisdom, that solvational changes are important in reactions of this type, but it should be borne in mind that the activities of $Co(en)_2Cl_2^+$ and the transition state will also change drastically on transfer from methanol to DMF, so that the net effect on ΔG^* will be relatively small. Furthermore, despite Langford's dissatisfaction with the facility of the argument, there is considerable evidence[8,52,121] (presented throughout the present review) that ΔG^* is insensitive to solvational influences, which show up in ΔH^* and ΔS^*.

(ix) Other types of free-energy relationships

Edwards[5] has attempted to correlate relative free energies of activation within a series of nucleophilic reactions involving a single substrate with a linear combination of the Brønsted basicities and the standard electrode potentials of the attacking reagents, and also with a linear combination of their relative polarizabilities (as measured by the molar refractivities) and proton basicities. These approaches seem to have been fairly successful with the square-planar Pt^{II} substrates, but, in the absence of sufficient data, it remains to be seen whether nucleophilicity in octahedral I_a mechanisms (as measured by the relative k_i values from eqn. (5)) can be treated in this manner. One cannot be optimistic, since steric factors are evidently important in octahedral substitution[45,139,140], but presumably a different order of nucleophilic powers of reagents toward Cr^{III} as compared with Pt^{II} (reflecting class "a" as opposed to class "b" behaviour) could be accommodated in the coefficients of Edwards' linear combinations.

For class "a" centres such as Cr^{III} and $Co(NH_3)_5{}^{3+}$, it may be anticipated that the Brønsted basicity of attacking (in I_a) or leaving (in I_a and I_d) groups would predominate over the polarizability or redox parameters in Edwards' correlations. Indeed, several linear correlations exist between the logarithms of aquation rate coefficients and the pK_a of the conjugate acid of the departing ligand for octahedral complexes of Cr^{III} and Co^{III}; the reader is referred to the recent review of this topic by Bakač et al.[150]. However, Asher and Deutsch[120] have argued that the correlations published by Monacelli[151] for the aquations of $Cr(NH_3)_5X^{2+}$ and $Cr(OH_2)_5X^{2+}$ are linear at low pK_a only because of a serendipitous choice of pK_a values for the strong acids HX, and that the correlation breaks down in the latter case at p$K_a \geqslant 2$ because X then separates as HX rather than X^-.

E. ENTHALPIES OF ACTIVATION, ΔH^*

(i) Relationships between ΔH^* and ΔH^0

Enthalpies of activation (or Arrhenius activation energies $E_a = \Delta H^* + RT$) are commonly considered to be more directly related to molecular parameters such as bond strengths than are ΔG^* values, and accordingly arguments concerning ligand-field effects on substitution kinetics and the application of functions of the Morse type to considerations of the attributes of various mechanistic models have generally been cast in terms of ΔH^* or E_a, rather than ΔG^*. However, it was noted in Section D that solvational changes can make substantial contributions[4,8,52,121] to ΔH^* and $T\Delta S^*$, whereas these contributions tend to cancel each other in ΔG^*. Thus, it is legitimate to set up Figs. 1—3 with pseudo-Morse curves on a *free-energy* scale, and it follows that any correlations extracted from such a diagram (in the absence of a detailed knowledge of the functional form of these curves) will involve only ΔG^* and ΔG^0.

Nevertheless, ΔH^* makes a far larger contribution to ΔG^* than does $T\Delta S^*$ in most slow octahedral substitutions, and it follows that the vertical axes of Figs. 1—3 could be relabelled in terms of enthalpy without much loss in realism. Accordingly, wherever a free-energy relationship exists, we can anticipate that an *enthalpy relationship* will also exist

$$\delta\ \Delta H^* = \alpha\ \delta\ \Delta H^0 \tag{24}$$

where α will be essentially the same for a given reaction as in the corresponding Brønsted plot, since it is determined by the geometrical properties of the pseudo-Morse curves of Figs. 1—3, which will be almost unchanged (or else changed in roughly the same way for ML_5X and ML_5Y) if the figures are redrawn in terms of enthalpies. Nor will the shapes and relative positioning of the Morse curves of ML_5X and ML_5Y in Figs. 1—3 be significantly affected by pressure or temperature, so that α should be effectively independent of T and P; indeed, if an LFER is to hold good at more than one temperature, the same type of relationship must exist between ΔH^* and ΔH^0 as exists between ΔG^* and ΔG^0. Thus, if we accept the existence of LFER's over at least some ranges of ΔG^0 for systems in which ΔH^* and ΔG^* are large relative to $T\Delta S^*$, it follows that linear enthalpy relationships must also exist and have slopes α which are the same as for the corresponding LFER's. In the event that a curved, rather than a linear, free energy relationship is observed, a similar curve can be anticipated for the enthalpy relation.

The essential requirement for the derivation of eqn. (24) from eqn. (13) is simply that α be sensibly constant over the ranges of T and P encountered in solution kinetics. Then, using the thermodynamic relationship

$$(\partial G/\partial T)_P = -S \tag{25}$$

$$\begin{aligned} -\delta\,\Delta S^* &= (\partial\ \delta\,\Delta G^*/\partial T)_P \\ &= \{\partial(\alpha\ \delta\,\Delta G^0)/\partial T\}_P \\ &= \alpha\ (\partial\ \delta\,\Delta G^0/\partial T)_P \end{aligned} \tag{26}$$

whence

$$\delta\,\Delta S^* = \alpha\,\delta\,\Delta S^0 \tag{27}$$

for which eqn. (24) follows, since

$$\partial\,\Delta G^* = \partial\ \Delta H^* - T\partial\Delta S^* \tag{28}$$

Equation (24) represents a linear enthalpy relationship if α does not change significantly from one member of the reaction series to another.

$$\Delta H^* = \alpha\ \Delta H^0 + \text{constant} \tag{29}$$

As with free-energy relationships, α is expected to be 1.0 for I_d processes, but close to 0.5 (and not strictly constant, if a wide enough range of ΔH^0 can be covered) for I_a mechanisms. The aquation of $Co(NH_3)_5X^{(3-n)+}$ should provide a test of the former statement, but unfortunately the spread of available ΔH^0 values[152] is limited and the uncertainties in ΔH^*_{CoX} and ΔH^0

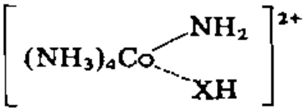
are large enough to obscure any conformity with eqn. (29). One might add Taube and Posey's data for $X^{n-} = SO_4^{2-}$ ($\Delta H^*_{CoX} = 18.7 \pm 0.5$, $\Delta H^0 = -3.7$ kcal.mol^{-1}), but work in our laboratories[154] and by Monacelli[155] has yielded a significantly higher ΔH^* value in this case (22.3 kcal.mol^{-1} at 25°C); this serves to illustrate the difficulty of assembling enough sufficiently reliable enthalpy data to test the existence of enthalpy correlations.

For an I_d process, the condition that α is unity means that the quantity ($\Delta H^*_{CoX} - \Delta H^0$), which Powell[152] refers to by the curious term "enthalpy of transition" (ΔH_T), but which according to Hess's Law and the Principle of Microscopic Reversibility is simply ΔH^* for the reverse reaction ($Co(NH_3)_5OH_2^{3+} + X^{n-}$), should be constant if $Co(NH_3)_5OH_2^{3+} - X^{n-}$ ion-pairing contributions to ΔH^0 and ΔH_T ($\sim$ 1 kcal.mol^{-1})[10] are properly allowed for. Powell[152] suggests that this is so for aquations of $Co(NH_3)_5X^{(3-n)+}$, with ΔH_T close to ΔH^* for aquo-exchange as expected, but here again the apparent variations in ΔH_T from one X to another are almost as great as the variations in ΔH^*_{CoX} itself.

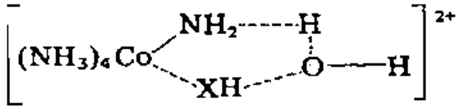
For the base hydrolyses of $(NH_3)_5CoX^{(3-n)+}$, data for $X^- = I^-$ can be included (since redox decomposition does not compete with base hydrolysis), and ion-pairing is less significant. Here, Powell's ΔH_T is fairly constant (31.9 ± 1.0 kcal.mol^{-1}) for $X^{n-} = Cl^-, Br^-, I^-, NO_3^-$ (ref. 156) and H_2O (using $\Delta H^0 = -4.5$ kcal.mol^{-1} for the acid ionization of $Co(NH_3)_5OH_2^{3+}$)[157]; for $X^{n-} = SO_4^{2-}$, we can calculate $\Delta H_T = 34.5$ kcal.mol^{-1} *, which is in fair agreement with the others considering the different ionic strengths ($I = 1.0$ M for SO_4^{2-}, 0.1 for the others) and the cumulative errors ($\sim \pm 1.5$ kcal.mol^{-1}). But here again, the scatter in ΔH_T values approaches that in ΔH^* for base hydrolysis and no clear conformity with the requirements of a dissociative mechanism can be claimed.

However, Table 1 shows that the difference $\Delta\Delta H^*$ between ΔH^* for base hydrolysis and ΔH^* for aquation of $Co(NH_3)_5X^{2+}$ is essentially the same (4.6 ± 0.4 kcal.mol^{-1}) for all the *strong-acid* anions $X^{n-} = Cl^-, Br^-, \underline{N}CS^-, NO_3^-$ and SO_4^{2-}, as is the corresponding $\Delta\Delta S^*$ (39.6 ± 2.8 cal.deg^{-1}.mol^{-1}). These data indicate that base hydrolysis rate coefficients are larger on the average by a factor of 2×10^5 M^{-1} than those for aquation at 25°C, and emphasize once again the close similarity between the rate-determining processes of these hydrolysis paths for Co^{III} ammines.

Marked deviations from the $\Delta\Delta H^*$ and $\Delta\Delta S^*$ norms are noted for the basic ligands $X^- = F^-$ and especially N_3^- (the more basic of the two in the Brønsted sense), and it seems likely that the structure of the transition state approximates to



or



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* From $\Delta H^* = 26.3$ for the base hydrolysis[158], $\Delta H^0 = -3.7$ for $Co(NH_3)_5SO_4^+$ aquation[153], and $\Delta H^0 = -4.5$ kcal.mol^{-1} for the acid dissociation of $Co(NH_3)_5OH_2^{3+}$ (ref. 157); in Table II of ref. 158, for 0.81×10^{-2} read 0.81×10^{-3}.

TABLE 1

Activation parameters for aquation and base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ ($I = 0.1$ *M* except as stated)

X^{n-}	$\Delta H^*(OH^-)$ (kcal.mol^{-1})	$\Delta H^*(H_2O)$	$\Delta\Delta H^*$	$\Delta S^*(OH^-)$ (cal.deg^{-1}.mol^{-1})	$\Delta S^*(H_2O)$	$\Delta\Delta S^*$	Ref.
F^-	25.6	24.4	1.2	+16.6	− 8.9	25.5	159, 160
Cl^-	28.1	23.3	4.8	+32.4	− 6.8	39.2	159, 160
Br^-	27.6	23.2	4.4	+35.4	− 3.8	39.2	159, 160
I^-	29.9	(19)		+46.4	(−16)		160, 161
NCS^-	35.2	30.1	5.1	+42.0	− 0.8	42.8	114
NO_2^-	37.4 [a]	30.0 [a]	7.4	+44.0 [a]	+ 5.8 [a]	38.2	162
NO_3^-	28.8	24.3	4.5	+43.1	+ 1.9	41.2	72
N_3^-	32.0 [a]	33.2 [a]	−1.2	+30.3 [a]	+13.1 [a]	17.2	16
SO_4^{2-}	26.3 [b]	22.3	4.0	+24.6 [b]	−10.9	36.5	154, 155, 158

[a] Zero ionic strength.

[b] $I = 1.0$ *M*.

TABLE 2

Thermodynamic and activation parameters for the acid-independent aquation of $Cr(OH_2)_5X^{(3-n)+}$ in 1.0 *M* perchlorate solution

X^{n-}	ΔH_0^* (kcal.mol^{-1})	ΔH^0 (kcal.mol^{-1})	ΔS_0^* (cal.deg^{-1}.mol^{-1})	ΔS^0 (cal.deg^{-1}.mol^{-1})	Ref.
H_2O	26.2	0.0	0.3	0.0	47
F^-	28.7	−4.2	− 3.9	−29.3	42, 164, 165
Cl^-	24.3	−6.0	− 7.1	−16	52, 108
Br^-	23.8	−5.1	− 3.5	− 5.0	52, 108
I^-	23.0	−7.6 [a]	− 0.2	− 2.6	52, 108
NCS^-	27.5	+ 2.1	− 3.5	− 6.9	52, 108
NO_3^-	21.6	−4.5	− 5.1	− 5.9	108, 166
SO_4^{2-}	21.9	−7.2	−13.0	−29.3	46, 106
HF	28.7	+ 8.0 [b]	− 3.9	+ 5.9 [b]	42, 167

[a] Measured at $I = 4.2$ *M*, assumed same at $I = 1.0$ *M*.

[b] Calculated for $Cr(H_2O)_5F^{2+} \rightleftharpoons Cr(H_2O)_5OH^{2+} + HF$.

in these two aquations but to simple X^- separation from $(NH_3)_4CoNH_2^{2+}$ in the base hydrolyses[53,159]. The nitro complex might be expected to behave as do F^- and N_3^-, but seems to be anomalous. The aquation of $Co(NH_3)_5I^{2+}$ is known to be complicated by redox processes[161], and Table 1 suggests that values of $\Delta H^* \simeq 25.3$ kcal.mol^{-1} and $\Delta S^* \simeq +7$ cal.deg^{-1}.mol^{-1} would be obtained if pure aquation could be observed.

For the aquation of $Cr(OH_2)_5X^{(3-n)+}$, Powell's[163] ΔH_T varies widely from one X^{n-} to another — that is, ΔH^* for the anation process depends markedly upon the nature of X^{n-}, as expected for an I_a mechanism. A plot of ΔH^* against ΔH^0 for the aquation reaction (Table 2) reveals a linear correlation of slope $\alpha = 0.4_5$ and intercept 26.5 kcal.mol^{-1} for $X^{n-} = NCS^-, H_2O, Cl^-, Br^-$ and I^-; as in Fig. 4, the correlation is poor for $X^{n-} = NO_3^-$ and not good for SO_4^{2-}. Furthermore, ΔH_{CrF}^* is over 4 kcal.mol^{-1} higher than the enthalpy correlation would predict; if ΔH^0 for the formation of $Cr(OH_2)_5OH^{2+}$ and HF is used in place of ΔH^0 for $Cr(OH_2)_6^{3+}$ and F^-, ΔH_{CrF}^* correlates better but is about 1.5 kcal.mol^{-1} *lower* than expected.

It seems likely that the transition state for aquations involving basic X^{n-} resembles $\{HX^{(n-1)-}$ + the conjugate base of $ML_5\}$ much more closely than $\{X^- + ML_5\}$, but that the proton in question forms a hydrogen bond between X^{n-} and the conjugate base, rather than an independent $HX^{(n-1)-}$ moiety[67]. This feature will influence ΔH_{MX}^* and $T\Delta S_{MX}^*$ primarily through anomalous solvation, and consequently these effects cancel[8,52,53,121,159] in ΔG_{MX}^*, so that $Cr(H_2O)_5F^{2+}$ correlates satisfactorily in Fig. 4, as do $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5N_3^{2+}$ in the LFER for the aquations[67] of $Co(NH_3)_5X^{(3-n)+}$.

(ii) Ligand field contributions to ΔH^*

The predominant factor determining the relative lability in substitution of octahedral complex ions of the same electronic configuration is the oxidation state of the central metal atom. Thus, ΔH^* for substitution in $Mn(OH_2)_6^{2+}$ is generally about 7—8 kcal.mol^{-1}, as against about 15 for $Fe(OH_2)_6^{3+}$ (ref. 2). However, for a given oxidation state, there is often a striking inertness toward substitution for the configurations d^3, d^8, and spin-paired d^5 and d^6. This has been attributed to the large loss of crystal-field (or ligand-field) stabilization energy which is expected to accompany the loss of a ligand, as in the D or I_d mechanisms, or on gaining a seventh ligand[2], as in I_a or A.

This ligand-field contribution to the activation energy (LFAE) should manifest itself in ΔH^* if no solvational contributions are involved, as in reaction (30); otherwise, it may be looked for in ΔG^*, in which solvational contributions to ΔH^* and $T\Delta S^*$ tend to cancel (Section E(i)).

$$M(OH_2)_6{}^{n+} + H_2{}^*O \rightleftharpoons M(OH_2)_5{}^*OH_2{}^{n+} + H_2O \quad (30)$$

Breitschwerdt[168,169] has shown that the experimental ΔH^* or E_a values for reaction (30) with M = Cr, Mn, Fe, Co, Ni and Cu ($n = 2$) are reproduced surprisingly well by crystal-field calculations assuming a dissociative mechanism proceeding via a square-pyramidal (C_{4v}) transition state; for a dissociative mechanism with a trigonal-bipyramidal (D_{3h}) or an associative one with a pentagonal-pyramidal (D_{5h}) transition state, the calculated E_a values are two to eight times too large. This is comfortably in accordance with the I_d-type mechanism assigned to substitutions in $M(OH_2)_6{}^{2+}$ by Eigen and Wilkins[170], and suggests that this type of calculation may have real significance for simple I_d processes.

Other improved versions of the original Basolo—Pearson LFAE theory[2] have been developed by Companion[171], who used many-electron rather than single-electron methods and improved crystal-field parameters; Yamatera[172], who utilized molecular-orbital methods involving second-order perturbation theory with allowance for π-bonding and -antibonding interactions; and Spees et al.[173], whose detailed treatment includes the assumption that the d-electrons of the central metal atom occupy the lowest available d-like antibonding molecular orbitals of the complex in the transition state even at the expense of spin-pairing (e.g. Cr^{III} is taken to be a doublet rather than a quartet d^3 system in the transition state).

However, when the theory of Spees et al.[173] is applied to the reaction

$$M(NH_3)_5{}^{18}OH_2{}^{3+} + H_2O \rightarrow M(NH_3)_5OH_2{}^{3+} + H_2{}^{18}O \quad (31)$$

LFAE values of 40, 87, 88 and 57 kcal.mol^{-1} are calculated for I_d (C_{4v} transition state), I_d (D_{3h}), I_a (C_{2v}) and I_a (D_{5h}) mechanisms when M = Rh; when M = Ir, the corresponding values[174] are 49, 105, 109 and 67 kcal.mol^{-1}.

These are all far in excess of the observed ΔH^* values of 24.6 and 28.1 kcal.mol^{-1} for M = Rh and Ir respectively, and furthermore suggest that an I_d (C_{4v}) mechanism should prevail in substitution reactions of these aquopentaammine complexes, whereas there is strong experimental evidence[174] in favour of I_a (C_{2v}).

Furthermore, Spees et al. calculate LFAE values of 30.1 and 35.2 kcal.mol^{-1} for I_a (D_{5h}) and I_a (C_{2v}) mechanisms in the aquo-exchange reaction of $Cr(OH_2)_6^{3+}$, on the assumption of a spin-paired (doublet) transition state, as against 47.3 and 55.7 for doublet I_d (C_{4v}) and I_d (D_{3h}), so that an I_a mechanism would appear to be favoured on this basis. This inference is in accordance with the experimental evidence documented throughout this review. However, if the corresponding calculations are made with the alternative assumption of spin-free (quartet) transition states, we find LFAE values of only 10.0, 28.6, 21.0 and 22.0 kcal.mol^{-1} for I_d (C_{4v}), I_d (D_{3h}), I_a (D_{5h}) and I_a (C_{2v}) transition states respectively, which suggests that the I_d (C_{4v}) mechanism should be favoured, contrary to the experimental evidence.

In summary, then, it seems that the role of ligand field effects in determining ΔH^* and mechanism is rather smaller than is commonly supposed where I_a processes appear to be involved. Indeed, one would not expect LFAE contributions per se to be more important than the isotropic force attracting the ligands to the positive metal centre in determining ΔH^*, yet this force has generally been ignored in attempts to calculate ΔH^*, as have solvent effects in cases where these are clearly significant. Thus, Strehlow[175] has pointed out that ΔH^* for water replacement in $Al(OH_2)_6^{3+}$ (in which ligand field effects are absent) would be over 100 kcal.mol^{-1} for an I_d process, although ΔH^* for anation by sulphate is only 22 kcal.mol^{-1} — a fact which he attributes to the operation of an I_a process. Nevertheless, it must be acknowledged that some significant correlations do exist in *dissociatively activated* octahedral substitution between ligand field parameters (as measured by the wavenumbers of *d—d* electronic absorption maxima) and kinetic reactivity, though the latter is better gauged by ΔG^* than ΔH^* if solvational changes are likely to be significant[4,176,177].

(iii) Solvent effects on ΔH^*

Bennetto and Caldin[11,178] have discovered some remarkable linear correlations existing between ΔH^* for the replacement of solvent ligands in Ni^{II} complexes in divers solvents by various standard nucleophiles and such measures of solvent structural properties as fluidity and heat of vaporization. Thus, the Eigen—Wilkins version of the I_d process evidently needs to be modified to take into consideration the new interactions between the displaced solvento-ligand and the surrounding solvent molecules when metal—solvent bond fission occurs.

Bennetto and Caldin[11,178] consider that ligand substitution processes involve *concerted* interactions of ligand and solvent molecules extending from zone (*d*) (defined in Section B) through (*c*), (*b*), into (*a*) and progressively out again to (*d*). We prefer to consider the complex with its first and second coordination spheres as being independent of bulk solvent on the timescale of the intimate substitution process; solvent-structure-related effects such as those revealed by Bennetto and Caldin[11,178] may then be understood if it is conceded that solvent molecule interactions within the second coordination sphere (zone (*b*)) of the complex are likely to be the same in general character as those in the bulk solvent — in fact, they may well be amplified by the presence of the polarizing central ion.

Bennetto and Caldin[11,178] also examine the question of the linear correlations of ΔH^* with ΔS^* ("isokinetic behaviour") which are frequently found for series of related reactions[11,65,111,177–181]. The existence of such correlations for series of reactions is a good indication that the essential reaction mechanism is the same throughout a given series; isokinetic behaviour indicates that ΔH^* and $T\Delta S^*$ are to a large extent mutually compensatory, and, as remarked above several times, this is a characteristic of solvation effects. This close compensation of $\Delta\Delta H^*$ and $T\Delta\Delta S^*$ can occur despite very complex changes in ΔH^* as a result of (e.g.) progressive changes in the solvent composition for the reaction of Ni^{II} with bipyridyl in aqueous methanol or methanolic acetonitrile[178]. At present, it is not clear whether much more information than the above can be extracted from isokinetic plots — for example, whether any special significance can be read into the slope of such a plot (the "isokinetic temperature").

F. ENTROPIES OF ACTIVATION, ΔS^*

ΔS^* is commonly regarded as a measure of the "increase in randomness" occurring on going from the initial state to the transition state, and it might therefore be expected to yield some useful mechanistic information. However, McGlashan's eloquent warning[182] concerning the naive interpretation of truly thermodynamic entropies of reaction (ΔS^0) in terms of changes in randomness applies with even greater force in dealing with ΔS^* data, which are merely quasithermodynamic quantities and which are usually calculated on the assumption that the transmission coefficient is unity. Furthermore, for any but unimolecular reactions, the absolute value of ΔS^* as commonly calculated will depend on the choice of concentration scale, and this leads to interpretational complications if the attacking reagent is the solvent. For these reasons, little significance can be attached to an *isolated* observation that ΔS^* happens to be zero or some other specific value for a reaction of a complex in solution.

However, for a series of related reactions in a given solvent, the *relative* values of ΔS^* should show some correlation with mechanism. For the aquo-exchange reactions of Table 3, ΔS^* is close to zero or slightly positive for all the ions listed except $Co(NH_3)_5OH_2^{3+}$, which evidently reacts by an I_d mechanism[183]; this is entirely consistent with our contention that all the

TABLE 3

Activation parameters for some solvent exchange reactions

Reaction	ΔH^* (kcal.mol^{-1})	ΔS^* (cal.deg^{-1}.mol^{-1})	ΔV^* (cm^3.mol^{-1})	Ref.
$Co(NH_3)_5OH_2^{3+}/H_2O$	26.6	+ 6.7	+ 1.2	183
$Rh(NH_3)_5OH_2^{3+}/H_2O$	24.6	+ 0.8	− 4.1	36
$Ir(NH_3)_5OH_2^{3+}/H_2O$	28.1	+ 2.7	− 3.2	174
$Cr(NH_3)_5OH_2^{3+}/H_2O$	23.3	0.0	− 5.8	36
$Cr(H_2O)_6^{3+}/H_2O$	26.2	+ 0.3 [a]	− 9.3	47
$Cr(DMSO)_6^{3+}/DMSO$	23.1	−15.4 [a]	−11.3	28

[a] Exchange of *one* ligand only.

others react by an I_a process, which perforce involves a higher degree of organization in the transition state than does I_d. For the $Cr(DMSO)_6^{3+}/DMSO$ exchange reaction, an I_a mechanism is evidently again operative, but ΔS^* is now strongly negative (so dispelling any lingering suspicions that any special significance may be attached to the near-zero value of ΔS^* for the I_a aquo-exchange processes); this strongly negative value probably reflects steric problems peculiar to DMSO as a ligand[28].

For complexes of the type $Cr(OH_2)_5X^{(3-n)+}$, Baldwin, Bracken and Keen [127–129,184] have shown that, for $X^- = Cl^-$, Br^- and $\underline{N}CS^-$, *four* of the aquo ligands exchange with solvent water with $\Delta S^* = 0 \pm 3$ cal.deg^{-1}.mol^{-1} per ligand, which is the same as has been observed[47] for $Cr(OH_2)_6^{3+}$ (ΔH^* is a little higher for the latter, and the rate correspondingly lower, as expected for a 3+ ion relative to a 2+). This suggests a common I_a process for all these exchanges. However, for $X^- = Cl^-$, Br^- and $\underline{N}CS^-$, the fifth ligands (presumably *trans* to X) exchange with ΔS^* in the range +14 to +22 cal.deg^{-1}.mol^{-1}, and the exchange rate is markedly greater than for the other aquo groups (presumed *cis*) despite somewhat higher ΔH^* values. This striking *trans*-activation therefore probably operates through a *dissociative* mechanism. A similar conclusion was reached by Pavelich and Harris[30], who have assigned a D mechanism to the powerful *trans*-labilizing effect of chloro and hydroxo ligands in pentaaquorhodium(III) complexes. Thus, our generalization, that cationic complexes of trivalent transition metals other than Co^{III} undergo substitution by I_a mechanisms, needs to be qualified by excluding complexes that exhibit strong *trans*-activation.

For aqueous $Cr(OH_2)_5SO_4^+$, Baldwin and Keen[127,128] found that a single, relatively rapid exchange rate applies for all five aquo groups, yet ΔS^* is strongly negative (~ −20 cal.deg^{-1}.mol^{-1}). This suggests that an aquo group *cis* to SO_4 can be expelled in an associative ring-closure movement leading to a transiently bidentate sulphato complex. This would labilize *all* the aquo groups, since SO_4 could move from one ligand site to another as it first chelates and then aquates back to monodentate, and the high degree of organization demanded by such a process would lead to a relatively strongly negative ΔS^* for the net aquo-exchange.

This last mechanism is precisely that which we have suggested, above and elsewhere[43,185], for substitution reactions at Cr^{III} when non-linear oxyanions are involved. It is important in that it places some severe limitations on the study of aqueous Cr^{III} chemistry, e.g. nitrate or sulphate should not be used to control the ionic strength or acidity in studies of the kinetics or steric course of substitutions at Cr^{III} centres[185]. Its operation at Cr^{III} centres probably reflects not only the vulnerability of Cr^{III} to I_a attack, but also its preference for very "hard" ligand atoms (in this case, O). For the latter reason, *cis*-activation by NO_3^- or SO_4^{2-} probably will not be important[155,186] at "soft" I_a-prone centres such as Rh^{III}.

(i) Relationships between ΔS^* and ΔS^0

Equation (27) shows that the same relationship should exist between ΔS^* and ΔS^0 as exists between ΔG^* and ΔG^0, if the Brønsted slope α is independent of temperature and pressure. Accordingly, if an LFER exists for a series of reactions, ΔS^* will also be a linear function of ΔS^0, with the same slope as the LFER. This may be confirmed from the data of Table 2 for the aquations of $Cr(OH_2)_5X^{2+}$, with some notable exceptions. The deviation of X = F from the linear entropy relationship can be ascribed to the separation of an entity[42] resembling HF rather than F^-, as explained in Sections D(v) and E(i), the correlation of $Cr(OH_2)_5F^{2+}$ in the LFER of Fig. 4 being due to the fortuitous cancellation of solvational entropy and enthalpy contributions. Other exceptions are the cases $X^{n-} = NO_3^-$ and SO_4^{2-}, which also deviate from the LFER (Fig. 4) for reasons given in Section D(v).

In the absence of ΔS^0 data for aquation reactions, one might use in their place values of the standard entropies of the released aqueous ions X^{n-} after correction ($\overline{S}^0_{corr}$) for rotational entropy lost by a polyatomic ion on coordination, since $\overline{S}^0$ values for the original complexes (say, $Cr(OH_2)_5X^{(3-n)+}$) will be closely similar for the various X^{n-} and the product complex is the same ($Cr(OH_2)_6^{3+}$) throughout a given series. The problem of estimating the rotational correction is virtually intractable, since some free rotation of polyatomic ligands is likely to persist in the complexed state, and interactions with the solvent are an unknown factor. However, a calculation of the rotational entropy for the gas phase seemed to suffice to estimate $\overline{S}^0_{corr}$ for $X^- = NO_3^-$ and NCS^- in the pentaaquochromium(III) series, and a good correlation between ΔS^* and $\overline{S}^0_{corr}$ was obtained[108], the slope being 0.53 (cf. 0.56 for the corresponding LFER)[52]. The abnormally positive ΔS^* values observed when X^- is the anion of a weak acid (N_3^-, F^- (ref. 108) or CN^- (ref. 187)) presumably reflect the separation of HX rather than X^- (Sections D(v) and E(i)). Unfortunately, the anomalies of $X^- = NO_3^-$ in the LFER (Fig. 4) and the $\Delta S^*/\Delta S^\circ$ correlation suggest that the fit of $Cr(OH_2)_5NO_3^{2+}$ in the $\Delta S^*/\overline{S}^0_{corr}$ relationship was to some extent fortuitous.

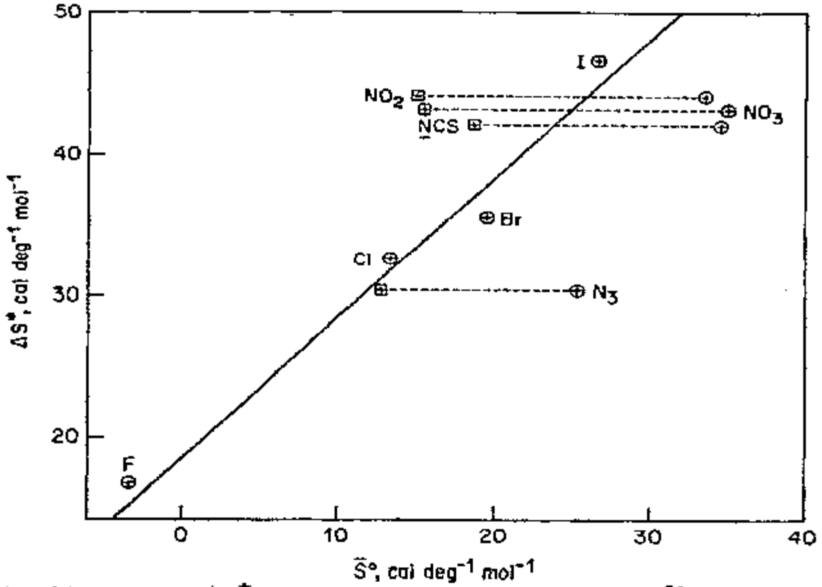

Fig. 5. Relationship between ΔS^* for base hydrolysis of $Co(NH_3)_5X^{2+}$ and the standard molal entropy $\overline{S}^0$ of aqueous X^-. Circles, $\overline{S}^0$ uncorrected for rotation; squares, gas-phase rotational entropy correction applied to $\overline{S}^0$. Data from sources cited in refs. 2 (p. 164), 72 and 108.

Furthermore, an attempt[108] to apply this same approach to the aquations of $Co(NH_3)_5X^{2+}$ suggested that the appropriate rotational correction is around 50 to 90% of the calculated gas-phase rotational entropy for NCS^-, NO_3^- and NO_2^-. Figure 5 shows an essentially linear correlation of unit slope between ΔS^* and $\overline{S}^0$ (corrected and uncorrected for rotation) for the base hydrolysis of $Co(NH_3)_5X^{2+}$. The fluoro and azido complexes are seen to behave "normally" in this case, whereas their ΔS^* values for the corresponding aquations are anomalously high; once again, this suggests that the leaving group in aquation resembles HF and HN_3 respectively[159], whereas in base hydrolysis F^- and N_3^- separate as such, since the cobalt ammine is already in the form of its conjugate base prior to Co—X bond breaking. This same rationale explains the fact that the difference $\Delta\Delta S^*$ between ΔS^* values for base hydrolysis and aquation of $Co(NH_3)_5X^{(3-n)+}$ (Table 1) is almost constant for all the X^{n-} listed except F^- and N_3^-; evidently, the activation process is similar in both aquation and base hydrolysis, with these exceptions, and the entropy contribution of conjugate base formation to $\Delta S^*(OH^-)$ is virtually independent of the nature of X^{n-}.

(ii) ΔS^* and stereochemical change in aquation

Tobe[189] has pointed out that ΔS^* is usually markedly larger (typically by about 15 cal.deg⁻¹.mol⁻¹ for *comparable* species) for aquations of complexes of the type $MLACl^{n+}$ (where L = $(en)_2$, trien, cyclam, etc., A is an "inert" ligand sich as NH_3 or CN^- and M = Co^{III} or Rh^{III}) when there is marked steric change than when the aquation is stereoretentive.

Studies by Kernohan and Endicott[83] on complexes of Co^{III} with macrocyclic ligands show that ΔS^* *can* be markedly positive for chloride aquation even when this is stereoretentive, probably because of extensive steric relaxation in the transition state (see also Chau and Poon)[190]. Nevertheless, for Co^{III} complexes with non-macrocyclic "garland" ligands, Tobe's rule seems to hold good if comparisons are made between sufficiently similar complexes. Thus, for *trans*-dichloro(1,4,8,11-tetraazaundecane)cobalt(III) ions, aquation of the *trans*-(*RR*,*SS*) isomer proceeds with steric change and $\Delta S^* = +12$ cal.deg^{-1}.mol^{-1}, whereas for the stereoretentive aquation[191] of the *trans*-(*RS*) isomer $\Delta S^* = +1$. This observation places Alexander and Hamilton's[192] observation of $\Delta S^* = +4$ cal.deg^{-1}.mol^{-1} for the stereoretentive aquation of *trans*-dichloro-(4,7-diaza-1,10-decane-diamine)cobalt(III) in proper perspective; as remarked at the beginning of Section F, the absolute magnitude of ΔS^* is singularly difficult to interpret, so that Tobe's rule should be applied only when comparisons are made between reasonably similar complexes. Further demonstrations of the validity of Tobe's rule have been given for cobalt(III) ammines[193] and ethylenediamine complexes[194].

Steric change at Co^{III} centres presumably occurs through rearrangement of the initially produced square-pyramidal five-coordinate intermediate to a trigonal-bipyramidal species. Theoretical calculations show that this process could not result in a change in the vibrational and rotational entropies of the simpler species such as $Co(NH_3)_4Cl^{2+}$ sufficiently large to account for the large ΔS^* relative to comparable stereoretentive reactions. Evidently the relatively positive ΔS^* reflects extensive desolvation of the square-pyramidal intermediate as it rearranges to the trigonal-bipyramidal form. It is noteworthy that the ΔS^* accompanying steric change in the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ is much larger at low ionic strengths, and is matched by a larger ΔH^*, as expected for solvational effects[193].

It may be that each of several solvating water molecules is doubly hydrogen-bonded through protons on two nitrogens *cis* to each other in the square-pyramidal intermediate, and that this bridging arrangement is disrupted when the ligands move apart towards the trigonal-bipyramidal configuration, with consequent loss of solvation[195]. Whatever the mechanism of desolvation, it would seem that some three to six water molecules would have to be shed if Powell's estimate[196] of the entropy change accompanying solvation (~ -3 cal.deg^{-1} per mole of water) is realistic.

G. HEAT CAPACITIES OF ACTIVATION, ΔC_p^*

Correlations involving ΔH^* (Section E) and ΔS^* (Section F) for series of related complexes have been sought for with the implicit assumption that these parameters are temperature-independent, so that one might legitimately compare data obtained over different temperature ranges. Yet if ΔH^* and ΔS^* bear any relation to the corresponding truly thermodynamic quantities, it must be acknowledged that they can both be temperature-dependent, i.e. that ΔC_p^* $(= (\partial \Delta H^*/\partial T)_p)$ can be non-zero. Indeed, it is now well established [197—199] that ΔC_p^* is significant for many organic solvolyses in aqueous media, typical mean values being −30 to −100 cal.deg^{-1}.mol^{-1} at 25°C, and that the effect probably originates in solute—solvent interactions involving the making or breaking of solvent structure.

Preliminary attempts to measure ΔC_p^* for the aquation of $Co(NH_3)_5X^{2+}$ yielded values not far removed from zero (− 44 cal.deg^{-1}.mol^{-1} for X = Cl (ref. 200) and − 20 ± 7 for $X = NO_3$ (ref. 72)), while values of zero[201], − 29 ± 3 (ref. 202) and − 17 ± 3 (ref. 202) cal.deg^{-1}.mol^{-1} have been obtained for chloride aquation in the *trans*-dichloro-, *cis*-chloroazido-, and *cis*-chloronitrobis(ethylenediamine)cobalt(III) ions. Thus, it can be reasonably assumed that ΔH^* (and also ΔS^*, since entropy can be defined in terms of heat capacity) is practically constant for the purposes of Section E and F.

However, a detailed study[203] recently completed in our own laboratories shows that if rate coefficients are measured with adequate precision over a wide enough range of temperatures (50° or more), the fact emerges that ΔC_p^* is itself unmistakably temperature-dependent. Thus, for the aquation of $Co(NH_3)_5Br^{2+}$, ΔC_p^* is strongly negative (~ − 100 cal.deg^{-1}.mol^{-1}) in the regions near 0° and 70°C, but reaches a maximum value of ~ − 10 cal.deg^{-1}.mol^{-1} near 35°C; the same is true for $Co(NH_3)_5SO_4^+$, although the reliability of the data in this latter case is somewhat reduced by the correction made for the small contributions of an acid-dependent pathway. The actual numerical values of ΔC_p^* obtained for various mean temperatures are not very significant, since their apparent value will depend upon the width of the temperature interval over which they are calculated (20° or more); any attempt to reduce these intervals below 20 − 25°C leads to numerical instability[203,204] of the equations used to calculate ΔC_p^*. In any event, any attempt to quantify the seemingly parabolic temperature dependence of ΔC_p^* would imply that significance can be attached to the *third* and *fourth* derivatives of the rate coefficients with respect to temperature, and this is unrealistic in the context of current experimental techniques.

Nevertheless, it is encouraging to note that Wold[204] has recently shown that ΔC_p^* is also generally strongly temperature-dependent in the hydrolyses of organic compounds, but in these cases a *minimum* is observed, once again near 35°*C* (it is tempting to speculate that mammalian body temperatures may be connected in some way with solute/solvent interactions in the bloodstream!). This qualitative difference in behaviour might be explained on the basis that neutral organic solutes promote water structuring in the initial state, by a presumed "buttressing" effect (clathrate-type hydration), while highly charged complexes with peripheral acidic protons will presumably be solvated by water molecules with the negative ends of their dipoles oriented towards the metal. Formation of large, low-charged ions in S_N1 hydrolysis of the organic compounds will probably result in net solvent structure-*breaking*, whereas in the case of the more highly charged complex ions an I_d process leads from a structure-forming substrate to a more powerfully structure-forming transition state (net structure-*making*).

The reason for the temperature dependence of ΔC_p^* is not clear at present, but we may note that minima *or* maxima can occur (again, near 35°C) in the standard heat capacity change ΔC_p^0 as a function of temperature for various ionization reactions, and a partial explanation for this effect has been advanced[205].

It would seem, then, that $|\Delta C_p^*|$ is serendipitously small and nearly temperature-independent in the ΔH^* or ΔS^* correlations for octahedral substitutions considered here, since the mean temperature involved in the measurements of these parameters was usually close to 35°*C*. A much more serious potential cause of variation of ΔH^* and ΔS^* with temperature is the occasional occurrence of *competitive* or of *sequential* reaction paths of comparable rates. Thus, if there are two competitive (parallel) reaction paths having the same apparent rate law but different ΔH^*, the path with the higher ΔH^* will predominate at high temperatures, and that with low ΔH^* under cooler conditions, so that the apparent ΔH^* will increase with temperature. This situation evidently obtains in the acid-independent aquation of the acetatopentaaquochromium(III) ion[206], in which ΔH^* varies from 13 kcal.mol^{-1} at 25°C to 33 kcal.mol^{-1} at 55°C. In all probability, the low-enthalpy path corresponds to C — O, and the high ΔH^* to Cr — O, bond breaking.

In the case of two consecutive steps of comparable rates, that of higher ΔH^* will be the "bottleneck" at low temperatures, and that with the lower ΔH^* will become rate-determining at high temperatures, so that the apparent ΔH^* will decrease with increasing temperature. We have suggested[60] that this may be the case in the homolytic decomposition of pyridiomethylpentaaquochromium(III) ion, but an independent experimental reinvestigation of this system would be welcome (see Section C(vi)). Perlmutter-Hayman[207] has considered the related case of a fast pre-equilibrium prior to the rate-determining step, and has shown that a large apparent $|\Delta C_p^*|$ can result in this situation.

H. VOLUMES OF ACTIVATION, ΔV^*

The volume of activation, ΔV^*, measures the change in partial molal volume which occurs on going from the initial state to the transition state, and is derived from the rate coefficient k by the relation

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \tag{32}$$

so that ΔV^* reflects the pressure dependence of k much as ΔH^* reflects its temperature dependence. However, the effect of the pressure P on k is relatively small compared with temperature effects, and ΔV^* can itself be strongly pressure-dependent, so that numerous careful rate measurements must be made if meaningful ΔV^* data are to be obtained. High-pressure methods are unfamiliar to most inorganic solution chemists, but are not particularly difficult, and can yield some unusual information regarding reaction dynamics; interested readers may learn about the technique, scope and limitations of pressure studies from the excellent monographs now available[208—210].

The value of high-pressure studies in elucidating inorganic reaction mechanisms is the subject of a recent review by Stranks[9], and need not be considered in detail here. The chief advantage of ΔV^* measurements in this context is that they are relatively easily understood in terms of atomic movements alone; the interpretation of ΔH^* and ΔS^*, on the other hand, involves less tangible factors such as molecular energy levels and the mode of occupation thereof. Volume changes on the macro scale are directly perceived by the human senses, whereas enthalpy and entropy are transcendent abstractions; thus, one may theorize about ΔV^* with much more confidence than in the cases of the other activation parameters.

It was explained in Section F that the absolute magnitude of ΔS^* has no immediately obvious significance per se. In constrast, the observation of a negative ΔV^* value in a substitution reaction tells us that a general contraction must occur on going from the initial state to the transition state; moreover, in the absence of solvational changes or other recognizable complicating factors, the negative ΔV^* value is diagnostic of an *associative* mechanism — it is very hard to see how a dissociative process, in which only bond-breaking is important, could lead to a negative ΔV^* unless some drastic increase in solvation occurs. Fortunately, solvational changes in aqueous solution reveal themselves in a marked pressure dependence of ΔV^*, as explained below, so that a negative, pressure-independent ΔV^* value is an excellent criterion of an associative mechanism (I_a rather than A, since in the latter case the solvation sheath would have time to reequilibrate with bulk solvent during the lifetime of the intermediate of expanded coordination number, so that pressure dependence of ΔV^* might be observed).

This is particularly well exemplified by ΔV^* values for solvent exchange reactions such as eqns. (30) and (31); here, there is no net chemical change, the entering and leaving groups being the same and also being the main (or the sole) species present in the second coordination sphere. It is found that $\ln k$ is a linear function of P within the experimental error in all such cases studied to date (Table 3), so that solvational changes are insignificant, and the interpretation of the ΔV^* data is straightforward and in full accordance with our tenet that, *of the cationic octahedral complexes of trivalent transition metals, only those of cobalt(III) undergo simple ligand substitution by a dissociative interchange mechanism*[174].

For Rh^{III}, Ir^{III} and Cr^{III}, the relatively large collapse in volume on going from the ground state to the transition state must originate in the removal of the incoming solvent molecule from the second coordination sphere and its implantation in the first with no more than a slight displacement of the ligand to be replaced — this is the essence of an I_a mechanism, and this mechanism is seen to prevail at Cr^{III} whether the "static" ligands be DMSO, NH_3 or H_2O or whether the solvent be H_2O or DMSO. Recognition of the fact that ΔV^* for an associative mechanism must include a large negative contribution due to removal of the incoming group from the second coordination sphere dismisses any doubt that the numerically small but distinctly positive ΔV^* for the $Co(NH_3)_5OH_2^{3+}$ aquo exchange (Table 3) results from an I_d mechanism.

The magnitudes of $-\Delta V^*$ for the I_a processes should therefore reflect the spatial extent of the second coordination sphere. Independent data such as are obtained from ion exchange chromatography[36] show that the *hydrated* radius of a complex ion of a given type will decrease as the "crystal" radius of the central metal ion increases; indeed, we see that $-\Delta V^*$ for aquo exchange in the pentaammines decreases in the order Cr > Rh > Ir, whereas the crystal radii increase $Cr^{3+} < Rh^{3+} < Ir^{3+}$ (ref. 174). Hexaaquo ions have more extensive solvation sheaths than pentaammines with the same central metal ion[36], and so we see that $-\Delta V^*$ is larger for $Cr(OH_2)_6{}^{3+}$ than for $Cr(NH_3)_5OH_2{}^{3+}$. $-\Delta V^*$ for solvent exchange in DMSO is larger than for the analogous process in water, since the DMSO molecule is much larger than H_2O, even though the latter forms voluminous solvation sheaths through hydrogen bonding[28].

For reactions in which there is net chemical change but no great solvation changes, we again find that positive ΔV^* values are associated with reactions expected on other grounds to be I_d or D (such as complexation of Ni^{II} by PADA)[211], while in Pt^{II} systems, long recognized as reacting by A mechanisms, negative ΔV^* values have been found[212]; similar correlations have been established for substitution reactions of transition metal carbonyls[213].

There is one case on record in which ΔV^* for aquo-exchange *may* involve solvation changes, viz. the isomerization of aqueous *trans*-$Co(en)_2(OH_2)_2{}^{3+}$, which is evidently preceded by I_d loss of an aquo ligand[214] and for which ΔV^* is strongly positive and pressure-dependent[9,215]. However, in the light of Tobe's association of desolvation with the rearrangement of a five-coordinate intermediate from tetragonal-pyramidal to trigonal-bipyramidal (see Section F(ii))[189,195], it seems likely that ΔV^* for the initial aquo-dissociation step may still be numerically small, positive and pressure-independent, just as for the $Co(NH_3)_5OH_2{}^{3+}$ aquo-exchange[183], and that the larger, pressure-dependent contribution to ΔV^* is associated with the actual rearrangement of the resulting five-coordinate species. This possibility is presently under investigation in our laboratories.

(i) Relationships between ΔV^* and ΔV^0

Following the approach taken in Section E(i) (eqns. (25) — (29)), and noting that

$$(\partial G/\partial P)_T = V \qquad (33)$$

the existence of a free-energy relationship

$$\partial\, \Delta G^{*} = \alpha\, \partial\, \Delta G^{0} \tag{34}$$

implies the existence of a volume relationship

$$\partial\, \Delta V^{*} = \alpha\, \partial\, \Delta V^{0} \tag{35}$$

having the same Brønsted slope α if this can be taken as being independent of temperature and pressure. Here, ΔV^0 is the net molar volume change for the completed reaction measured under the same conditions of ionic strength, temperature and pressure as ΔV^*. In practice, ΔV^* is markedly pressure-dependent (as ΔV^0 must also be) when solvational changes are involved, as explained below. Accordingly, it is convenient to correlate the extrapolated value ΔV_0^* of the activation volume at zero or atmospheric pressure (these are indistinguishable, in high-pressure studies) with ΔV^0 measured by conventional means such as dilatometry at ambient pressure.

If α is constant (or approximately so) for a given series of reactions, then eqns. (34) and (35) become an LFER and a linear volume relationship respectively, the slope α being the same in each. This holds true for the aquation[216] of $Co(NH_3)_5X^{(3-n)+}$, where the mechanism is I_d and so $\alpha = 1.0$ (see Table 4). Insufficient data are presently available to permit construction of a free-energy plot for $Cr(NH_3)_5X^{(3-n)+}$ aquations, but a linear volume relationship of $\alpha = 0.59$ can be drawn[45] for these reactions from the data of Table 4. This again is as would be anticipated for an I_a mechanism (see Section D), and the contrast with the I_d-activated cobalt(III) system may be illustrated by plotting corresponding ΔV_0^* values for the two series against each other[45].

The extent of these correlations is limited by extraneous factors, such as the problem of ammine ligand loss in the Cr^{III} series (especially where *cis*-activation by coordinated oxyanions can occur[43,185]), the incursion of redox phenomena[161] as in the case of $Co(NH_3)_5I^{2+}$, or difficulties in the direct determination of ΔV^0 when the reaction is very slow. The latter problem could be obviated for the Co^{III} series by measuring the conventional partial molal volumes $\bar{V}^0$ of $Co(NH_3)_5X^{(3-n)+}$, $Co(NH_3)_5OH_2{}^{3+}$ and X^{n-}; the last are mostly available already[217,218] and a parallelism may be noted between $\bar{V}^0$ and ΔV_0^* (Table 4), even though $\bar{V}^0$ for the parent complex must also vary markedly with X^{n-}. Thus it transpires that $Co(NH_3)_5NCS^{2+}$ would probably fit the linear volume correlation, but ΔV_0^* for $Co(NH_3)_5N_3{}^{2+}$ is likely to be $\sim$ 25 cm^3. mol^{-1} too positive — again, this suggests that HN_3 is the leaving group rather than $N_3{}^-$ (Section E(i)), so that *desolvation*, rather than electrostriction of solvent, occurs on going to the transition state, with a consequent increase in volume.

(ii) Pressure dependence of ΔV^*

Experience shows that ΔV^* for reactions of complex ions is pressure-dependent when a change in solvation is expected to occur on going to the transi-

TABLE 4

Values of ΔV_0^*, x and ΔV^0 for aquations of $M(NH_3)_5X^{(3-n)+}$ [a]

M	X^{n-}	ΔV_0^* ($cm^3.mol^{-1}$)	x	ΔV^0 ($cm^3.mol^{-1}$)	V^0 [b] ($cm^3.mol^{-1}$)
Co	SO_4^{2-}	−18.5	8.0	−19.2	14.0
	Cl^-	−10.6	4.1	−11.6	17.8
	Br^-	−9.2	3.9	−10.8	24.7
	NO_3^-	−6.3	1.9	−7.2	29.0
	NCS^-	−4.0			35.7
	H_2O	+1.2	0.0	0.0	
	N_3^-	+16.8	−4.2		25.0
Cr	Cl^-	−10.8	1.9	−8.4	17.8
	Br^-	−10.2	2.0	−7.2	24.7
	I^-	−9.4	1.7	−6.0	36.2
	H_2O	−5.8	0.0	0.0	

[a] In general, $I = 0.1$ M, $T = 25°C$, $P = 1$ bar. Data from refs. 45, 183 and 216. See text for explanation of symbols.

[b] Partial molal volumes of X^{n-} relative to H^+ at 25°C and $I = 0$ (from ref. 217).

tion state, but that no significant variation of ΔV^* with pressure seems to occur for simple solvent exchange reactions, in which no changes involving *bulk* solvent need occur prior to reaching the transition state[9,28,36,45,47,174,183,216]. One can regard ΔV^* as being made up of two parts

$$\Delta V^* = \Delta V_b^* + \Delta V_s^* \tag{36}$$

where ΔV_b^* represents the virtually pressure-independent contribution of bond-making and -breaking and ΔV_s^* is the contribution of solvational changes. ΔV_s^* is pressure-dependent because solvent in the second coordination sphere is much less compressible than is bulk solvent; thus, although transfer of solvent from the bulk solution to the second coordination sphere results in large decreases in volume (~ -3 cm^3 per mole of water[216]) at low pressures, this change diminishes as the pressure is increased because the free solvent becomes almost as compacted as the electrostricted solvent. The result is that $|\Delta V_s^*|$ decreases as P increases, whether ΔV_s^* be positive or negative. Stranks[9] has examined this problem theoretically.

The choice of an appropriate analytical function to represent the pressure dependence of ΔV^* has been considered at length by Golinkin et al.[219], who have shown that, for organic solvolyses at least, ln k is usually best represented simply by a quadratic in P.

$$\ln k = \ln k_0 + BP + CP^2 \tag{37}$$

Here, B is $-\Delta V_0^*/RT$, and $(\partial \Delta V^*/\partial P)_T$ is taken to be constant and so equal to $-2RTC$. This approach also works well with complex ion reactions in aqueous solution[9,45,216], but if we assume the electrostricted water to be completely incompressible we can gain some physical insight (with, if anything, an improved fit of the data) by adapting the Wohl—Tait equation[220] for the compression of water to calculate ΔV_0^* and x, the number of water molecules apparently added to the second coordination sphere from bulk solvent as we go from the initial to the transition state[45,216].

$$\ln k_p = \ln k_0 - P\Delta V_0^*/RT - (18.0\,x\rho/2.303RT)\,[(\pi + P)\ln(1 + P/\pi) - P] \quad (38)$$

Here, ρ and π are parameters of water known from ordinary compressibility measurements ($\rho = 0.321$, $\pi = 3.06$ kbar at 25°C)[167], and typical values of x obtained in least-squares computer fits of data to eqn. (38) are listed with the corresponding ΔV_0^* values in Table 4. The ΔV_0^* are close to those obtained with eqn. (37). The x values so obtained are actually *lower limits* to the increase in the number of water molecules in the second coordination sphere, and should be increased slightly (by some 10%, on the basis of Strank's theory[9]) to correct for the fact that electrostricted water is not entirely incompressible. This approach is somewhat analogous to that used by various authors to obtain solvation numbers of ions in solution from compressibility measurements[221—223].

Two interesting observations emerge from the x values of Table 4. First, the aquation of $Co(NH_3)_5N_3^{2+}$ is clearly seen to involve extensive *desolvation* on going to the transition state, just as has been inferred on independent grounds (Section E(i)). Secondly, for the same X^{n-}, the increase in solvation of $Cr(NH_3)_5X^{(3-n)+}$ on going to the transition state during aquation is only about *half* that of $Co(NH_3)_5X^{(3-n)+}$, as expected on the basis of an I_a mechanism at Cr^{III} and an I_d at Co^{III}.

I. CONCLUSIONS

For a series of substitution reactions of related octahedral complexes proceeding via a common I_d mechanism, linear correlations of slope $\alpha = 1.0$ should exist between ΔG^* and ΔG^0, ΔH^* and ΔH^0, ΔS^* and ΔS^0, and ΔV^* and ΔV^0. For solvent exchange reactions, ΔV^*should be positive and independent of pressure. In anation reactions (governed by eqn. (5)), k_i will not exceed k_{ex} and will be almost independent of the nature of the incoming group. D mechanisms may be distinguished from I_d on the basis of the products of competition reactions. These characteristics are exemplified by substitution reactions of Co^{III}.

For I_a mechanisms, α should be less than 1.0 and should change monotically over an extensive series of related reactions, but, where $\Delta G^* \gg \Delta G^0$, seemingly linear relationships of slope α near 0.5 will normally be observed between ΔG^* and ΔG^0, ΔH^* and ΔH^0, ΔS^* and ΔS^0, and ΔV^* and ΔV^0. ΔV^* for solvent exchange will be negative and independent of pressure. For anation reactions, k_i *may* exceed k_{ex} if the nucleophilicity of the incoming group toward the given central metal ion exceeds that of the solvent, but in any event k_i will be strongly dependent upon the nature of the incoming ligand. All these characteristics have been observed in simple substitution reactions of Cr^{III}, and several in those of Rh^{III} and Ir^{III}.

Those reactions which exhibit the above I_a characteristics are also rigorously stereoretentive[185], in accordance with flanking rather than remote attack by the incoming group relative to the displaced ligand. Stereochemical change is associated with I_d, D and D_{cb} mechanisms only, though not with all such processes.

Deviations from the patterns of activation parameters so established are associated with anomalous mechanisms. Where these anomalies are essentially solvational, as when the separating ligand in aquation is the conjugate base of a weak Brønsted acid, no marked deviation may be observed in the ΔG^* correlation, in which large anomalies in ΔH^* and $T\Delta S^*$ tend to cancel. Some Cr^{III} and Rh^{III} complexes can undergo substitution by a D mechanism as a result of *trans*-activation, while for Cr^{III} complexes at least, base hydrolysis and "induced aquation" proceed by essentially dissociative processes, much as for Co^{III}. *Cis*-activation by anions coordinated to Cr^{III} can also lead to anomalous kinetic parameters, but this process is probably of an associative type involving transient chelation.

The temperature dependence of ΔH^* and ΔS^* for octahedral substitution in water can evidently be ignored in general, since the mean value of ΔC_p^* is small in the temperature ranges normally involved. However, ΔC_p^* itself shows a marked temperature dependence in aquations of Co^{III} ammines, rising from strongly negative values at the extremes of the normal liquid range of water to a maximum near 35°C. The pressure dependence of ΔV^* is a measure of the number of solvating water molecules gained (or lost) by the complex from bulk solvent on going to the transition state.

While the Eigen—Wilkins interpretation[170] of the substitution kinetics of typical *divalent* first-row transition metal complexes in terms of an I_d mechanism is not contested, the combination of data on the kinetics, stereochemistry and products of simple substitution reactions (that is, excluding base hydrolysis and *trans*-activated reactions) of cationic octahedral complexes of *trivalent* transition metals are fully consistent with the operation of an I_a mechanism for all cases examined in detail to date, except for cobalt(III) complexes (I_d). Data on vanadium(III)[224], molybdenum(III)[225] and ruthenium(III)[226] substitutions support this generalization, in addition to the cases of chromium(III), rhodium(III) and iridium(III) which have been considered at length above. For iron(III), too, it is apparent that k_i (eqn. (5)) for anation of the hexaaquo complex in water is dependent upon the nature of the incoming ligand[227], as expected for an I_a process.

The question of the systematics of substitution in iron(III) complexes has been studiously avoided thus far in this article, despite an abundance of kinetic data[227]. This is because measurements of the high rates of substitution of high-spin iron(III) complexes are inevitably less accurate than the approaches advocated in this review require; not only must relatively imprecise flow methods be resorted to, but the high acidity of the $Fe(OH_2)_6{}^{3+}$ ion in water results in the incursion of conjugate base reaction pathways even at high $[H^+]$. The latter factor also introduces the very strong possibility that anation of $Fe(OH_2)_6{}^{3+}$ by X^- actually occurs by attack of HX on $Fe(OH_2)_5OH^{2+}$, when HX has a pK_a greater than about zero[116]. Nevertheless, it is noteworthy that the rates of reaction of $(H_2O)_5FeOH^{2+}$ with X^{n-} in water are independent of the nature of X (for a given n, within the experimental uncertainty), whereas those of $Fe(OH_2)_6{}^{3+}$ with X^{n-} vary considerably[227] with X, as expected for D_{cb} and I_a processes respectively.

Recently, Devia and Watts[228] have argued, primarily on the basis of solvent activity coefficients, that the anation of hexakis(dimethylsulphoxide)iron(III) ion by thiocyanate in DMSO solvent proceeds by an I_d mechanism, yet they note that k_i (eqn. (5)) is essentially equal to k_{ex} (for DMSO exchange) at 25°C and must be more than twenty times *larger* than k_{ex} at 100°C — facts which indicate an I_a mechanism, just as for the analogous reaction of chromium(III)[2
The Devia—Watts approach may be taken as evidence against an A mechanism in the iron(III) system, but it probably cannot distinguish between I_d and I_a.

Our somewhat heretical hypothesis, that a change in the general mechanism of simple substitution in octahedral cations from I_d to I_a occurs on going from divalent to trivalent transition metals (other than cobalt), is actually entirely reasonable in terms of simple concepts of mechanistic preferences based on the charge density at the metal centre[229]. The charge density may be gauged by the charge/radius ratio, and is therefore much greater on M^{III} centres relative to M^{II} by virtue of their markedly smaller ionic radii[143,144] as well as their higher oxidation state. Thus, even though I_d processes may be universal for M^{II} substitutions, I_a mechanisms can be anticipated for M^{III}, M^{IV}, etc.

The problem with this interpretation is then to explain the anomaly of cobalt(III). (Ironically, cobalt(III) substitutions have long been assumed to typify reactions of M(III) complexes in general!) This anomaly probably reflects the fact that the spin-paired Co^{3+} ion has the smallest crystal ionic radius of all the trivalent transition metals[174], and it is known[139] that severe steric strain exists even in the ground state of such a simple complex as $Co(NH_2CH_3)_5Cl^{2+}$. Accordingly, steric compression will favour dissociative and suppress associative processes in Co^{III} complexes.

J. POSTSCRIPT

Since this article was written, Dr. R.A. Jackson (University of Sussex) has drawn the author's attention to the existence of linear "Polanyi relationships" between E_a and ΔH^0 for several series of gas-phase radical transfer reactions[230]. The similarity between these and eqns. (13) and (24) will be apparent, and their theoretical basis is presumably similar to that developed in Section D(iv). Thus, for the abstraction of H atoms from alkanes by radicals $\dot{R}$, the slope α of the Polanyi plot is 1.0 for $R = NF_2$, 0.86 for $R = Br$, 0.49 for $R = CH_3$, and zero for $R = F$ (since E_a is itself zero in this case)[230].

Finally, a recent paper by Espenson and Leslie[231] confirms our suspicions (Section C(vi)) that the recombination rate of Cr^{2+} and $\dot{C}H_2C_5H_4NH^+$ estimated in ref. 60 is too low; the reasons for this discrepancy are not clear at present, but the qualitative aspects of our proposed homolytic mechanism[60] seem to remain valid.

ACKNOWLEDGEMENTS

I thank Dr. R.A. Jackson and Professor M.L. Tobe for stimulating discussions, Dr. H.W. Baldwin for permission to quote his experimental results in advance of publication, and the National Research Council of Canada for financial support of our work in this field since 1965.

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