

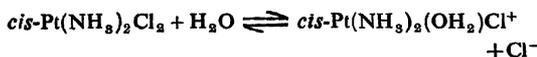
Dynamics of Ligand Substitution in Metal Complexes : A Survey of Studies on Octahedral and Square-Planar Complexes in Solution

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In connection with any chemical reaction two kinds of information are of vital importance viz. (i) *how far* a reaction would proceed and (ii) *how fast* will it reach the goal i.e. the dynamics of the process. The former is governed by thermodynamic and the latter by kinetic considerations. However, the recognition of the importance of kinetic aspects of inorganic reactions is a fairly recent one. Some forty years ago inorganic chemists used to correlate the failure of a substance to undergo a change with inherent stability of the substance. This was based on the then prevailing misconception that unlike the 'slow' organic reactions the inorganic reactions are 'instantaneous'. While this is true for the vast majority of simple inorganic reactions, e.g. reactions between ions forming an insoluble product thus leading to the formation of a precipitate, combination between H^+ and OH^- ions forming water (for which the rate constant as measured¹ by the pressure-jump relaxation technique is now known to be $1.5 \times 10^{11} M^{-1} sec^{-1}$ at $25^\circ C$), and so on, it was later recognised that many of the inorganic reactions are also very slow. Thus, aquation of $Ir(NH_3)_5I^{2+}$ involving replacement of the bound iodide by H_2O in acid solution has a rate constant of $1.9 \times 10^{-10} sec^{-1}$ at $25^\circ C$.² Our present state of knowledge on the mechanistic aspects of ligand substitution in octahedral and square-planar complexes is presented below.

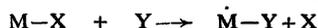
A striking illustration of the importance of kinetics and equilibria in inorganic systems is that of the behaviour of the *cis* and *trans* isomers of $Pt(NH_3)_2Cl_2$.³ The conductance of an aqueous solution of the *cis* isomer slowly increases with time and at equilibrium (after ca. 24 hr. at $25^\circ C$) the solution contains ca. 90% of the aquation product as ascertained by titration of the released chloride and the measured value of the conductance :



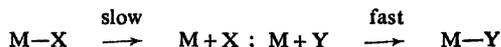
In contrast, the *trans* isomer remains unchanged under this condition. In presence of alkali, however, Cl^- is released slowly by both the isomers at rates independent of OH^- concentration and in agreement with this the rate of release of Cl^- from the *cis* isomer in aqueous solution in absence of alkali is the same as that observed in presence of alkali. Furthermore, at $25^\circ C$ the rate of Cl^- release from the *trans* isomer is about 3 times faster than that from the *cis* isomer. Thus, despite the fact that the *trans* isomer is more labile than the *cis* isomer for aquation, the equilibrium is unfavourable for formation of the *trans*-chloroaquo product in aqueous solution while this is greatly favoured in the case of the *cis* isomer. In the presence of alkali, however, the reaction of the *trans* isomer also proceeds due to transformation of the chloroaquo complex into the chlorohydroxo complex in an acid-base reaction with OH^- and this prevents the back reaction that occurs in absence of alkali. Incidentally it may be mentioned that the higher rate of the *trans* isomer is in keeping with the well-known *trans-effect* sequence $Cl^- > NH_3$ and this was the first

unequivocal evidence that the *trans-effect*⁴ is kinetic in nature.

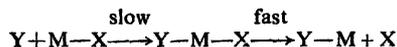
Ligand substitution reactions involving replacement of a ligand by another ligand constitute an important class of reactions of metal complexes which are of great utility in synthetic and analytical procedures and on which considerable rate studies have been reported during the last thirty years that have led to valuable information for understanding of the mechanisms of such processes. For a ligand substitution process



two distinctly different types of mechanisms are possible :



In such a process the rupture of the metal-ligand bond $M-X$ is primarily important in the transition state and following Ingold's notation for organic reactions such a mechanism is called S_N1 (substitution, nucleophilic, unimolecular) for which Langford and Gray⁵ have proposed the terminology **D** process (*dissociative* process). Alternatively, formation of the $M-Y$ bond may be primarily important in the transition state without any significant rupture of the $M-X$ bond :



This is a bimolecular nucleophilic substitution process, S_N2 which Langford and Gray calls **A** process (*associative* process). However, **D** and **A** processes

are limiting situations and in many systems there may be different degrees of M—X bond rupture and M—Y bond formation in the transition state which have been designated by Langford and Gray as *interchange* processes (I process). Interchange processes may have a variety of transition states, but two well-defined types will be those representing the transition states of A and D types of reactions which are denoted as I_a and I_d respectively. I_a processes will display substantial bonding to both the entering (Y) and leaving (X) groups. In I_d process there is weak bonding to both the entering and leaving groups.

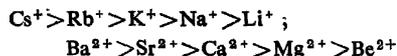
Using simple electrostatic arguments it is possible to speculate what would be the influence of the changes in sizes and charges of the central metal ion, the entering groups, the group being displaced and the non replaceable ligands on the rate of the three possible processes viz. D, I and A. The summary of the predictions as given in Table 1 is based on broad generalizations and considerations that the important features of D and A mechanisms are bond-breaking and bond-formation, respectively, whereas in an interchange (I) process bond-breaking and bond-formation are of comparable importance (*concerted* process).

TABLE 1—EFFECTS OF SIZES AND CHARGES ON RATES OF DISSOCIATIVE, INTERCHANGE AND ASSOCIATIVE REACTIONS

| Changes | Effects on rate | | |
|--|-----------------|---------------|-----------|
| | D process | I process | A process |
| Increase in positive charge of central atom | decrease | little change | increase |
| Increase in size of central atom | increase | increase | increase |
| Increase in negative charge of entering group | no effect | increase | increase |
| Increase in size of entering group | no effect | decrease | decrease |
| Increase in negative charge of leaving group | decrease | decrease | decrease |
| Increase in size of leaving group | increase | little change | decrease |
| Increase in negative charge of non-replaceable group | increase | little change | decrease |
| Increase in size of non-replaceable ligands | increase | little change | decrease |

The effect of charge and size of the central metal ion on the lability is elegantly demonstrated in the isoelectronic series having the lability sequence $AlF_6^{3-} > SiF_6^{2-} \gg PF_6^- > SF_6$ where increasing charge of the central atom gives rise to an increase in metal-ligand bond strength and consequent increase in inertness (decreasing lability) so much so that PF_6^- hydrolyzes extremely slowly and SF_6 is extremely

inert to hydrolysis in contrast to AlF_6^{3-} and SiF_6^{2-} which are hydrolyzed 'instantaneously'. Similarly, the studies of Eigen⁶ on 'fast' water exchange rates of aquametal ions show that the rate of exchange decreases with increasing cationic charge in the sequence $Na^+ > Mg^{2+} > Al^{3+}$. When the size of the metal ion decreases but the charge remains constant then a decrease in rate is observed, e.g. in the water exchange rates of hydrated metal ions the following orders have been observed :

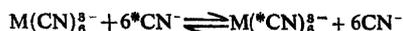


These observations are consistent with a dissociative mechanism.

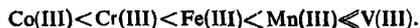
In order to review the developments which have taken place in the field of mechanisms of ligand substitution reactions of metal complexes it would be convenient to discuss the mechanistic features of the two most representative classes of coordination complexes viz. octahedral (such as complexes of Cr(III), Co(III), Rh(III), Ir(III), Pt(IV), etc.) and square-planar (such as complexes of Pd(II), Pt(II), Au(III), etc.). An exhaustive review on the ligand replacement processes in octahedral complexes of metals in oxidation state 3 has been published recently⁷.

Octahedral Complexes :

For comparable reactions of analogous complexes of metal ions of any particular transition series considerable variation in reactivity has been observed. Thus, for the following ligand exchange reactions of octahedral complexes of trivalent metal ions of the first transition series,

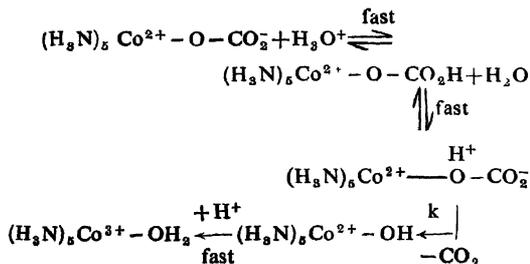


studied with cyanide ion (labeled with ^{13}C) in the solution the following order of increasing lability (increasing rate) has been reported^{8,9} :

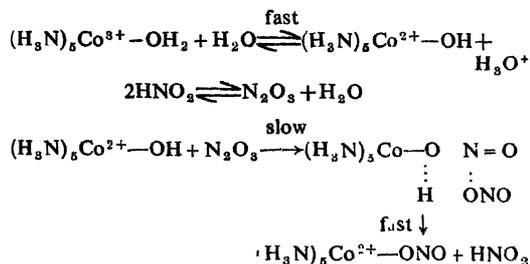


An attempt was made by Taube¹⁰ to interpret such observations on the basis of the valence bond theory as was applied by Pauling¹¹ to account for the bonding in metal complexes. Taube suggested that all outer orbital complexes, as also those inner orbital complexes having one or more vacant *d* orbitals (in the penultimate valence shell), might be expected to be labile; while those inner orbital complexes in which each of the *d* orbitals of the penultimate valence shell are filled with at least one electron should be inert. The observations reported above are fully in accord with this view. The reasonings put forth by Taube envisage a displacement mechanism for the inner orbital complexes and a dissociation mechanism for the outer orbital complexes. The presence of a low energy vacant *d* orbital is, therefore; essential for lability in the case of inner orbital complexes.

A much more successful approach to the problem has been made by an application of the ligand field theory¹². In this the loss in the ligand field stabilization energy (LFSE) accompanying the formation of the reaction intermediate (transition state) is believed to contribute to the activation energy of the process. The magnitude of this effect can be estimated from simple theoretical considerations, and greater the magnitude of this ligand field contribution (ΔE_a) to the activation energy (E_a) of the reaction the more inert will be the system. Based on this the predicted order of increasing lability for octahedral complexes is fairly in accord with the experimental observations. Also, the observed differences in the activation energy for identical reactions of analogous complexes of transition metal ions agree fairly well with those predicted by the ΔE_a values expressed in terms of appropriate Dq values¹³. These predictions are however not valid for ligand substitution reactions which occur by a pseudo-substitution process without any cleavage of the metal-ligand bond, as in the extremely rapid acid catalyzed decomposition of carbonatopentaamminecobalt(III) ion¹⁴ :



That no fission of the Co—O bond takes place in this reaction has been demonstrated by carrying out the reaction in water enriched in ¹⁸O when no uptake of ¹⁸O in the product has been observed¹⁵. This test is successful in this case because the exchange of $(\text{H}_3\text{N})_5\text{Co}(\text{OH}_2)^{3+}$ with water is exceedingly slow¹⁶. Another interesting case of pseudo-substitution is the formation of the thermodynamically less stable red coloured nitropentaamminecobalt(III) ion in over 80 percent yield by the action of $\text{HNO}_2 - \text{NO}_2^-$ buffer on aquopentaamminecobalt(III) ion at low temperature (ice bath)¹⁷ :

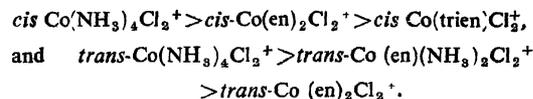


That no cleavage of the Co—O bond takes place has been confirmed by studies using ¹⁸O enriched aquo

complex when ¹⁸O is found entirely in the product nitrito complex¹⁸. With a knowledge of this reaction mechanism it has been possible to synthesize the previously unknown nitrito complexes of Rh(III), Ir(III) and Pt(IV)¹⁹. The extremely fast aquations of $\text{Cr}(\text{NH}_3)_5(\text{ONO})^{2+}$ and $\text{Cr}(\text{OH}_2)_5(\text{ONO})^{2+}$ also occur by pseudo-substitution processes without Cr—O bond cleavage²⁰.

The replacement of an anionic ligand by a molecule of water in acidic aqueous solution (pH < 5) is called *aquation* while the corresponding reaction occurring in basic media leading to replacement of the anionic ligand by OH⁻ is known as *base hydrolysis*. Various evidences point to the conclusion that reactions of Co(III) complexes proceed generally by dissociative mechanism, while the corresponding reactions of Cr(III) and particularly those of Rh(III) are associative in character.

A comparison of the rates of aquation of a series of Co(III) complexes of the type $\text{Co}(\text{NH}_3)_5\text{X}$ has shown²¹ that the rate decreases in the order of increasing thermodynamic stability of the complex and increasing affinity of Co(III) for X. Also significant is the observation of Lalor and Long²² that for aquation of several Co(III) complexes of the type $\text{Co}(\text{NH}_3)_4\text{X}^{2+}$ the activation energy increases linearly with the average ligand field strength of these complexes in the following sequence of X⁻ : Br⁻ < NC₃⁻ < NCS⁻ < NO₂⁻. It has further been observed²³ that increasing chelation such as replacing two NH₃ ligands by one ethylenediamine and four NH₃ by a molecule of triethylenetetramine, slows down the rate of aquation in a progressive manner in the sequence

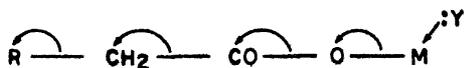


Also, the divalent monochloro complex $\text{cis } \text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$ reacts about 100 times slower than the monovalent $\text{cis } \text{Co}(\text{en})_2\text{Cl}_2^+$ complex²³. Again, in complexes of the type $\text{trans } \text{Co}(\text{AA})_2\text{Cl}_2^+$ where AA stands for ethylenediamine and C-substituted ethylenediamines (with —CH₃ replacing H in the —CH₂— groups) the rate of aquation is greatly increased progressively with more and more crowding due to alkyl substitution in the —CH₂— groups²⁴. All such observations as mentioned above are compatible with a dissociative mechanism.

Posey and Taube²⁵ observed that in the formation of $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ from $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ induced by metal ions in water enriched in ¹⁸O the product had the same ¹⁶O/¹⁸O ratio when Hg²⁺ was used to withdraw X⁻ (= Cl⁻, Br⁻, I⁻) showing that a common intermediate results in this case as is evidently possible for a dissociation mechanism in which $\text{Co}(\text{NH}_3)_5^{3+}$ is formed as an active intermediate. However, when Ag⁺ or Tl⁺ were used to assist in the removal of X⁻ the ¹⁶O/¹⁸O ratio varied with the nature of X⁻ suggesting that in these cases there is significant bond formation by the

incoming water molecule before complete dissociation of the Co—X bond. Since only the more reactive Hg^{2+} generates a common intermediate, $Co(NH_3)_5^{\ddagger+}$, it was concluded that uncatalyzed aquation of $Co(NH_3)_5X^{2+}$ occurs by a mechanism which is not purely dissociative but in which there is solvent participation in the transition state.

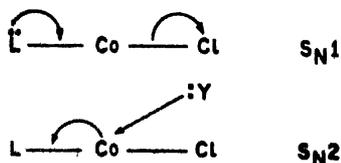
For complexes where X^- is acetate or substituted acetate ions, where basicity of the ligands differed by a factor of 10^4 suggesting a comparable difference in the strength of the Co—X bond the rates differed²⁶ only by a factor of ca. 10 which is also not compatible with a purely dissociative mechanism where Co—X bond rupture is only of importance. The authors²⁶ also observed that for the same complexes the plot of $\log k_{OH}$ vs. $\log K_a$, where k_{OH} is the second order rate constant for base hydrolysis of the complex and K_a is the dissociation constant of HX , is a good straight line indicating that the weaker base is also dislodged at the fastest rate (as in the case of aquation) but the spread in the k_{OH} values is much greater (a factor of ca. 100 as against ca. 10 for the aquation). This is reasonable on the basis of an associative mechanism since with decreasing basicity of the ligand (increasing electron withdrawing character of R_3CCOO^- , maximum for F_3CCOO^-) the attack by an anionic nucleophile like OH^- will be much more facilitated than by a polar non-ionic nucleophile such as H_2O :



For aquation of $trans-Co(en)_2(NH_3)X^{2+}$ the activation energy increases in the sequence of $X^- = Cl^- < Br^- < NO_3^-$ and the rate increases in the same order due to increasingly favourable entropy of activation which is compatible with a solvent-assisted dissociation mechanism²⁷. The case of $Co(NH_3)_5X^{2+}$ is parallel. The basic feature of the solvent-assisted dissociation mechanism is that dissociation of the Co—X bond is assisted by the solvent which in favourable cases is hydrogen bonded to the departing ligand and in the transition state as the Co—X bond is elongated and finally breaks off the H_2O molecule slips into the position vacated by the departed ligand. Deuterium substitution in the complex and the solvent slows down the rate of aquation of $Co(NH_3)_5Cl^{2+}$ and the results are said to be in agreement²⁸ with the solvent-assisted dissociation mechanism. However, the validity of this argument has been questioned²⁹. Further support to this solvent-assisted dissociation (SAD) mechanism comes from the observations³⁰ on the effect of D_2O on the rate of solvolysis of $Cr(NH_3)_5X^{2+}$. In these cases the variation in the rate of hydrolysis (aquation) is primarily due to the ΔS^\ddagger term, since ΔH^\ddagger values are practically the same for $X^- = Cl^-, Br^-$ and I^- . This means that the energy expended in the Cr—X bond rupture must be at least partially offset by a compensating solvation of the incipient halide ion, i.e., the solvent may be considered as one competing with the metal ion for the halide. On changing from H_2O to D_2O there is a slight increase in ΔH^\ddagger while there is a much greater

effect on ΔS^\ddagger term. Chloride, the most solvated halide in the series Cl^-, Br^- and I^- is released relatively slowly in D_2O compared to water than I^- (which is the least solvated halide³¹). Since ΔS^\ddagger for reaction parallels the entropy of solvation of the halide being released it is evident that solvation of the releasing halide is important in the transition state suggesting solvent-assisted dissociation. The observed acceleration of the rate of aquation of $Cr(NH_3)_5X^{2+}$ by various anions (polyvalent anions producing a more marked acceleration than monovalent anions) and the dependence of the effect of such ions on the total ionic strength (an increase in ionic strength retards the reaction) has been interpreted in terms of a solvent-assisted dissociation of an ion-pair formed between the complex cation and the accelerating anion. As a result of increase in the electron density in Cr(III) in the ion-pair dissociation of the Cr—X bond is facilitated while simultaneously the water molecule, which is hydrogen bonded to the bound X^- and the NH_3 in *cis* position to X^- , slips into the position vacated by X^- .

Ingold, Nyholm, Tobe and others³² have investigated the behaviour of *cis*- and *trans*- $Co(en)_2(L)X$. From their results it is now known that the nature of L determines the mechanism of substitution of X^- by H_2O . Electron donating groups (π -donors) like OH^- , N_3^- , Cl^- , Br^- , NCS^- for L lead to dissociative (S_N1) reaction, while others which are either π -electron acceptors (like NO_2^- or CN^-) or which are incapable of forming π -bonds (e. g. NH_3) lead to associative (S_N2) reaction :

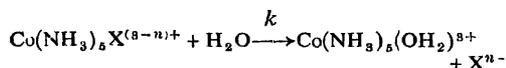


It has further been observed that for ligands promoting S_N1 reaction the *cis* isomer reacts faster (*cis*-effect) than the *trans* isomer, while the reverse is true for π -acceptor ligands promoting S_N2 process. Also, S_N1 reactions proceed with retention of configuration in case of the *cis*, but with rearrangement in the case of the *trans* isomer, while there is retention in both cases for S_N2 reaction. These can be readily understood³³.

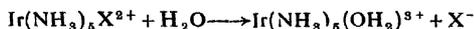
From a consideration of the group replacement factor ($GRF = k_{R-X}/k_{R-Cl}$) values for the aquation (and also of base hydrolysis) of the Co(III) and Cr(III) complexes of the type $M(NH_3)_5X^{2+}$ ($X^- = \text{halide}$) Chan *et al*³⁴ concluded that the observed sequence of GRF values viz. $F \ll Cl < Br < I$ rules out purely associative mechanism and is compatible with both the dissociative mechanism as also the interchange mechanism in which bond-making and bond-breaking are synchronous and of comparable importance. (For a purely associative mechanism the GRF values are expected to be in the sequence $F \gg Cl > Br > I$.) But the spread in GRF value is much greater for Cr(III)

(particularly in base hydrolysis) compared to Co(III) and this suggests a greater degree of bond fission in the case of Cr(III). However, this conclusion regarding Cr(III) is contrary to most other evidences, but the result that the reactions are not purely associative in character is compatible with other findings.

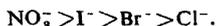
Another useful criterion is the *linear free energy relationship (LFER)*. The use of *LFER* plots to estimate the position of the transition state along the reaction coordinate has been discussed in theoretical terms^{3,5}. For the aquation reaction



the plot of $\log k$ vs $pK^{(a)}$, where K is the equilibrium constant for the reaction, is a straight line of slope = 1 for $\text{X}^{n-} = \text{NCS}^-$, F^- , H_2PO_4^- , Cl^- , Br^- , I^- and NO_3^- (only I^- and NCS^- are slightly off the line)^{3,5}. It has later been shown that $\text{X}^{n-} = \text{azide}^{3,7}$ and $\text{X}^{n-} = \text{nitrite}^{3,8}$ also fit into the *LFER* plot and for $\text{X}^{n-} = \text{SO}_3^{2-}$ and $\text{C}_2\text{O}_4^{2-}$ the *LFER* line is parallel^{3,9} to the *LFER* line for the univalent anions as X^{n-} . This linear free energy relation with a slope of unity of the *LFER* plot suggests that the nature of X in the transition state resembles its nature in the product (i.e. solvated X^-) indicating a dissociation mechanism in which $\text{Co}-\text{X}$ bond rupture is virtually complete in the transition state. This, however, does not tell us unambiguously about the role of the entering water molecule, but following an argument by Hammond^{4,0} it appears logical to conclude that the water molecule is only weakly bonded, if at all, in the transition state. Data^{4,1} for the system



also fit into a *LFER* plot with a slope of nearly unity (about 0.9) ; the observed reactivity order is



In contrast, for the aquation of $\text{Cr}(\text{OH}_2)_5\text{X}^{2+}$ ($\text{X}^- = \text{F}^-$, NCS^- , Cl^- , Br^- , I^-) the corresponding *LFER* plot has a slope of 0.56 which has been interpreted^{4,2} to signify that the separation of X^- from the Cr(III) centre is only about 50-60 percent complete in the transition state so that there is only partial bond breaking and the mechanism is perhaps one in which this bond-breaking and bond formation by the incoming water molecule are synchronous (interchange mechanism).

Jones and Swaddle^{4,3} have reported that for the aquation of $\text{Co}(\text{NH}_3)_5\text{X}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^- , SO_3^{2-}) the volumes of activation (ΔV^\ddagger) are equal (within experimental uncertainty) to the molar volume change (ΔV)^{4,4} for the respective completed reactions supporting Langford's conclusion based on *LFER* (*loc. cit.*). A large negative volume of activation ($\Delta V^\ddagger = -9.3 \text{ cm}^3 \text{ mol}^{-1}$) for the water exchange process for $\text{Cr}(\text{OH}_2)_5^{3+}$ has been presented as an evidence for an associative

mechanism^{4,5}, while the value of $\Delta V^\ddagger = 1.2 \text{ cm}^3 \text{ mol}^{-1}$ for the corresponding reaction of $\text{Co}(\text{OH}_2)_5^{3+}$ is consistent with a dissociative mechanism^{4,6}. The ΔV^\ddagger value of $16 \text{ cm}^3 \text{ mol}^{-1}$ for the aquation of $\text{Cr}(\text{NCS})_5^{2-}$ is also indicative of a dissociative mechanism^{4,7}.

A knowledge of the enthalpy of transition (ΔH_T), being the enthalpy difference between the transition state and the product (i.e. $\Delta H_T = \Delta H - \Delta H^\ddagger$), is also useful in the assignment of mechanism. A constant ΔH_T value of ca. 25 kcal mole⁻¹ for aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X}^- = \text{Cl}^-$, Br^- , NO_3^-) and water exchange of $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ supports a common transition state in all these cases^{4,8}, since only then can the ΔH_T value be independent of the nature of the departing ligand as here we are concerned with the enthalpy change in the transformation of the transition state to the product. Hence, this result supports a dissociation mechanism with $\text{Co}(\text{NH}_3)_5^{3+}$ as the Co(III) species in the transition state. The same criterion has been applied to $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ systems^{4,9}, as well as in $\text{Cr}(\text{OH}_2)_5\text{X}^{2+}$ systems^{5,0}.

Adamson *et al*^{5,1} have made use of crystal field considerations in the assignment of reaction mechanisms. In this approach the change in the *CFSE* and interelectronic repulsion energy in the formation of the transition state has been considered as giving a fair estimate of the activation energy for the substitution reaction. The activation energies for the aquation reactions of a number of Co(III) and Cr(III) complexes have thus been calculated for reactions occurring through each of the four different possible intermediate structures, viz. square pyramid (C_{4v}), trigonal bipyramid (D_{3h}), pentagonal bipyramid (D_{5h}) and trapezoidal octahedron (C_{2v}) and compared with the experimental values for the assignment of reaction mechanisms and also inferring about the structures of the intermediates in the different cases. It has been concluded in this manner that the aquation of several complexes of Cr(III) occur through a pentagonal bipyramid intermediate (hence associative mechanism), while similar complexes of Co(III) possibly react through a square pyramid intermediate (dissociation mechanism) although the possibility of the reaction proceeding through the pentagonal bipyramid intermediate could not be excluded.

The aquation of *cis*- $\text{Cr}(\text{en})_2\text{Cl}_2^{5,2}$ and of *trans*- $\text{Co}(\text{dmgH})_2\text{Cl}_2^{5,3}$ ($\text{dmgH}_2 = \text{dimethylglyoxime}$) in aqueous solution (in the absence of any added salts or acids) have been studied by the present author. In both the cases the ΔS^\ddagger values for the rate-determining release of Cl^- ion are nearly identical to the entropy of solvation of Cl^- in water from which it has reasonably been concluded that the reaction proceeds by an essentially dissociation mechanism which is assisted by solvation of the Cl^- being released ("SAD" mechanism, *loc. cit.*).

Important mechanistic conclusions can often be obtained from rate studies in solvents other than water

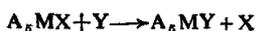
(a) Essentially this is a plot of free energy of activation vs standard free energy of reaction.

as well as in various solvent mixtures. Asperger and coworkers^{5,4} studied the substitution of Cl⁻ by thiocyanate in *trans*-Co(en)₂(NO₂)Cl⁺ and *trans*-Co(en)₂Cl₂²⁺ in different non-aqueous solvents and obtained evidences for a dissociation (S_N1) mechanism in the case of the dichloro complex and a different mechanism for the chloro-nitro complex. For the latter the rate is acid independent, while there is retardation by acid in the case of the dichloro complex with a limiting rate at high acid concentration. Both reactions are only slightly dependent on SCN⁻ concentration. In the case of the dichloro complex the rate in different solvents increases exponentially with the dielectric constant of the solvent suggesting S_N1 mechanism, while for the chloro-nitro complex no such regular trend is observed. This with the different nature of the effect of acid suggests a different mechanism in this case.

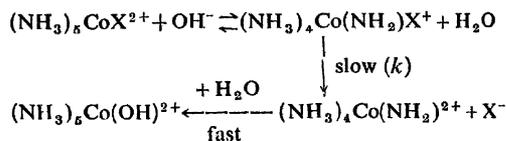
A detailed picture of the mechanism of aquation of Cr(NCS)₃³⁻ has emerged from a kinetic and NMR study of this reaction in acetonitrile. This solvent solvates the complex preferentially, so that the concentration of water in the solvation shell is small and controllable, and the composition of the solvation shell can be monitored by NMR relaxation technique⁵⁵. The dependence of solvolysis rate on solvent in a range of pure solvents indicates a dissociative mechanism. The study of rates as function of solvent composition in aqueous acetonitrile provides the details of the I_a mechanism. Rates and activation parameters for aquation of Cr(NCS)₄(en)⁻ in aqueous methanol mixtures have been determined. Results are consistent with "SAD" mechanism in which the amount of solvent assistance is small⁵⁶.

Logarithms of rate constants for aquation of *cis*-Co(en)₂Cl₂²⁺ correlate linearly (slope, *m*=0.35) with the Grunwald-Winstein solvent *Y* values for the methanol-, ethanol-, acetone-, dioxan-, formic acid-, and acetic acid-water solvent mixtures containing between 0 and 40 percent by volume of the non-aqueous component. This result is consistent with a dissociative mechanism for aquation⁵⁷. Aquation of Co(NH₃)₆Cl²⁺ and of *trans*-Co(en)₂Cl₂²⁺ in a similar range of aqueous-organic solvent mixtures has led to *m* values of 0.25 and 0.35 respectively. In fact, for a wide range of Co(III)-amine-chloride complexes the *m* values lie between 0.23 and 0.36 suggesting that for all these dissociative aquations there is a similar pattern of dependence of rate constant on solvent composition which can be characterized by an *m* value of around 0.3. For the Co(III)-amine-bromide complexes⁵⁸ the *m* values are around 0.2. This lower value for the bromo complexes compared to the chloro complexes is the same pattern as observed in the substitution reactions (organic) of alkyl halides.

In a majority of cases it is known that for an overall reaction of the type



the rate is independent of *Y*. Only in the case of *Y*=OH⁻ a first order dependence of rate on OH⁻ concentration has been observed in many cases. For the acidoamine complexes Basolo, Pearson and their coworkers⁵⁹ developed, based on Garrick's original idea, what is known as the conjugate base (CB) mechanism :



Here the conjugate base reacts by dissociation (S_N1) mechanism and is therefore denoted as S_N1CB. The extremely weak acidity (*pK_a* ~ 14) of such ammine complexes allows the concentration of the conjugate base to be extremely low even at fairly high OH⁻ concentration to lead to a perfect first order dependence of rate of base hydrolysis on OH⁻ concentration. That the rate of base hydrolysis is very much faster (by several powers of 10) is chiefly due to the pi-donor character of the -NH₂ group which would facilitate the loss of X⁻ from the *cis* position of -NH₂ and formation of the trigonal bipyramid intermediate in which strong ligand to metal pi-bonding can occur. This is comparable to the *cis*-effect of OH⁻, Cl⁻ and other such ligands capable of ligand to metal pi-bonding⁶⁰. Observations on the chloride exchange of the gold(III) complex Au(Et₄dien)Cl²⁺ (Et₄dien = Et₂N-CH₂CH₂-NH-CH₂CH₂-NEt₂) and its conjugate base Au(Et₄dien-H)Cl⁺ have shown that the latter is ca. 70 times more reactive⁶¹.

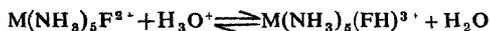
A consideration of the ratio of the rate constants for base hydrolysis and aquation of complexes of different trivalent transition metal ions shows that Co(III) and Ru(III) are very much more labile to base hydrolysis than Cr(III) and Rh(III).

| | | | |
|---|---------------------|---------------------|---------------------|
| M(NH ₃) ₆ Cl ²⁺ : Cr(III) | Rh(III) | Co(III) | Ru(III) |
| <i>k</i> _{OH} / <i>k</i> _{H₂O} : 2 × 10 ⁹ | 4 × 10 ³ | 5 × 10 ⁶ | 5 × 10 ⁶ |
| (25°C) | (90°C) | (25°C) | (25°C) |

In order to account for this observed order (viz. Ru(III) > Co(III) >> Cr(III) >> Rh(III)) of labilities to base hydrolysis on the basis of the conjugate base mechanism in all the cases one has to make a rather improbable assumption that the acidities (*pK_a* values) of the amines of these trivalent metal ions differ very widely. However, an attempt has been made to account for the observed labilities on the basis of the conjugate base mechanism⁶² and in contrast to Co(III) an S_N2CB mechanism has been suggested for Ru(III). An indirect evidence which has frequently been adduced in support of the conjugate base mechanism is the observation^{63,64} that even cationic complexes having no ionizable protons undergo base hydrolysis at a rate independent of OH⁻ concentration and in these cases the aquo product formed by usual aquation is transformed into the hydroxo complex in

An S_N1 dissociation mechanism has been suggested⁷⁷ in the case of $\text{Co}(\text{CN})_5(\text{S}_2\text{O}_3)^{4-}$ on the basis of experimental evidences.

Aquations of metal complexes which contain ligands (such as F^- , NO_2^- , N_3^- , CN^- , CO_3^{2-} , SO_4^{2-} , HPO_4^{2-} , SO_3^{2-} , oxalate, malonate, acetylacetonate, biguanide, etc) which can be protonated even in the metal-bound state are generally catalyzed by acids. Thus, in contrast to the behaviour of $\text{M}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) the aquation of $\text{M}(\text{NH}_3)_5\text{F}^{2+}$ is acid catalyzed due to formation of a conjugate acid (CA) :

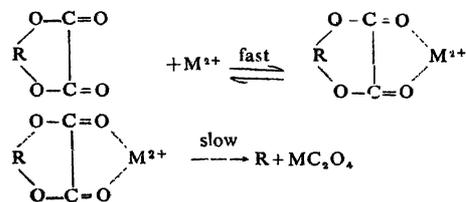


The conjugate acid then transforms into the aquo product by either an S_N1 or S_N2 process which are, therefore, known as $S_N1\text{CA}$ and $S_N2\text{CA}$ mechanisms respectively. In many such cases the rate has been found to be faster in D_2O than in H_2O due to the fact that D_3O^+ in D_2O is a stronger acid than H_3O^+ in H_2O indicating a fast protonation pre equilibrium before the rate step⁷. Formation of a conjugate acid as an intermediate is also possible in the case of ethylenediamine and 2,2'-dipyridyl due to one-ended dissociation of these chelating ligands so that protonation occurs at the "free" end of the ligand. This is, however, precluded in the case of 1,10-phenanthroline where because of three fused rings the structure is rigid and no free rotation about the C—C axis joining the two pyridine rings (as is possible in the case of 2, 2'-dipyridyl) is possible here and in this case, therefore, one-ended dissociation is not possible. Hence, while the dissociation of $\text{Fe}(\text{dipy})_2^{2+}$ to $\text{Fe}(\text{dipy})_2(\text{OH}_2)_2^{2+}$ occurs partly by an acid-catalyzed path⁷⁹ this is absent in the case of $\text{Fe}(\text{phen})_3^{2+}$. A large volume of work has been carried out in the present author's laboratory on the acid catalyzed reactions of metal complexes such as $\text{Cr}(\text{NH}_3)_5(\text{ONO})^{2+}$ ⁷¹, $\text{Cr}(\text{NH}_3)_5(\text{N}_3)^{2+}$ ⁷³, $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$ ⁸¹, several oxalato^{82,83}, malonate^{83,84} and acetylacetonate⁸⁵ complexes of Cr(III), Co(acetylacetonate)₃⁸⁶, several biguanide and N-substituted biguanide complexes of Cr(III)⁸⁷, Co(III)⁸⁷, and Rh(III)⁸⁸, oxalato-biguanide complexes of Cr(III)⁸⁹, Co(phen)₂(OX)₂⁹⁰, etc. Kinetic information also made possible the syntheses of several complexes of Cr(III)⁹¹. The possibility of protonation of the chelated biguanide prior to opening of the chelate ring leads to some apparently paradoxical results. Thus, both for Cr(III) and Co(III) and for any particular series (*tris* or *bis*) of complexes of the biguanides the rate decreases in the following sequence of decreasing basicity of the ligands although stability of the complexes decrease in the same sequence: Biguanide > n-Hexylbiguanide > Phenylbiguanide. This is because protonation of the chelated ligand which facilitates the cleavage of the metal-ligand chelate ring is expected to be less favoured in the same sequence as the decreasing basicity of the "free" ligands. Again, although ethylenediamine forms much less (thermodynamically) stable complexes with Cr(III) and Co(III) compared to biguanide, the ethylenediamine complexes are much

more inert (kinetically) than the corresponding biguanide complexes because protonation (which facilitates metal-ligand chelate ring cleavage) cannot occur prior to opening of the chelate ring in the case of ethylenediamine complexes due to absence of any "free" basic group in the chelated ethylenediamine⁸⁷. Thus, while for $\text{Cr}(\text{BigH})_3^{3+}$ the ΔH^\ddagger value is 10.1 kcal mole⁻¹, the corresponding value for $\text{Cr}(\text{en})_3^{3+}$ is 24.3 kcal mole⁻¹, and Co(BigH)₃³⁺ suffers dissociation in acid medium at a measurable rate at room temperature (ca. 30°C) while Co(en)₃³⁺ remains completely unchanged in 1M HClO₄ even for months at 30°C⁸⁷.

An insight into the mechanism of transformation of the conjugate acid (protonated form of the complex) into the product (i.e. the role of water in the transition state for the reaction in aqueous acid solution which tells us whether the reaction is $S_N1\text{CA}$ or $S_N2\text{CA}$) has been obtained from various evidences in some cases^{83,84,88}; the observed dependence of the rate on H^+ ion concentration and various acidity functions has been particularly useful^{83,88}.

Electrophilic catalysis by metal ions (similar to catalysis by H^+ ions) has also been reported^{25, 92-100} as also electrophilic catalysis by HNO_3 ^{97,103}. Catalysis of aquation of *ci*- $\text{Cr}(\text{Ox})_2(\text{OH}_2)_2$ into $\text{Cr}(\text{Ox})(\text{OH}_2)_4$ by several M^{2+} ions of the first transition series in acid media has been investigated by the present author¹⁰⁰ and the results have shown that $\log k_M$ (k_M being the rate constant for the metal ion catalyzed path) varies linearly with $\log K_{\text{MOx}}$ (K_{MOx} being the stability constant of the monooxalato complex of M^{2+}); the reactivity sequence being $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$. This suggests the operation of the following mechanism :



where R is $\text{Cr}(\text{Ox})(\text{OH}_2)_2^+$ moiety.

Similar results have now been obtained in our laboratory in the case of $\text{M}(\text{BigH})_3^{3+}$ ($\text{M} = \text{Cr}, \text{Co}$).

Several examples of nucleophilic catalysis are also known such as base catalysis in the dissociation¹¹⁰ of $\text{Ni}(\text{dipy})_3^{2+}$, reformation¹¹⁰⁽¹¹⁾ of $\text{Co}(\text{EDTA})^-$, and dissociation⁸⁷ of $\text{Cr}(\text{BigH})_3^{3+}$, formation of $\text{Cr}(\text{II})$ -EDTA complex in the reaction of several complexes of Cr(III) with EDTA in alkaline media¹¹¹, etc. In some such cases OH^- acts as a positive catalyst in accelerating the reaction, while in other cases it acts as a negative catalyst in retarding the reaction, the mechanisms of which have been elucidated. Incidentally, mention may be made that the reactions of square-planar complexes such as $\text{Pd}(\text{EigH})_2^{2+}$ ¹¹² and $\text{Pt}(\text{Ox})_2^{2-}$ ¹¹³ in aqueous solutions containing acid and halide ions exhibit both electrophilic catalysis by H^+ ion and nucleophilic catalysis by halide

ion. Based on kinetic data it was possible to isolate¹¹⁴ Pd(BigH)₂ (unknown so far) and study its conversion¹¹² into PdCl₂²⁻. A similar situation exists in the reaction of Pt(Ox)₂²⁻ with thiocyanate¹¹⁵.

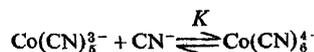
The formation of a metal complex in aqueous solution involving replacement of aqua ligands from an aquo complex has been extensively studied. It is now fairly well-established that these reactions involve outer-sphere association between the two reacting species in which the incoming ligand is generally believed to occupy a solvent site in the outer solvation sphere of the substrate aquo complex. The transformation of this outer-sphere complex into the product may then proceed by either a dissociative D or I_d or associative (A or I_a) path. In the cases of octahedral complexes the mechanisms are generally D, I_d or I_a, while A process is almost exclusively found in the reactions of some square-planar complexes (to be discussed later) which have a definite tendency to add additional ligands to increase the coordination number of the central metal ions in these complexes. In the majority of cases of octahedral complexes the interchange mechanisms operate in which bond-formation by the incoming ligand and cleavage of the M-OH₂ bond are synchronous. Such a mechanism has in fact been proposed by Eigen¹¹⁶ and used by others for the reactions of labile aquometal ions Cr(OH₂)₆³⁺ has been found to react¹¹⁷ with a variety of anions of strong acids at widely different rates, indicating significant incoming ligand participation in the transition state; the slope of the LFER plot of ΔG vs. ΔG[‡] also suggests some associative character (I_a mechanism). In contrast, the range of rates of reaction for Cr(OH)₂(OH₂)₅²⁺ with the same series of ligands is small, which suggests a predominantly dissociative mechanism. Earlier work¹¹⁸ however has shown that the reactions of Co(NH₃)(OH₂)₅³⁺ with various ligands (X) are fairly insensitive to the nature of X (X = Cl⁻, Br⁻, NO₃⁻, NCS⁻, H₂PO₄⁻, NH₃) with rate constants in the range of 1.3 × 10⁻⁶ to 2.5 × 10⁻⁶ M⁻¹ sec⁻¹ (at 25°C) as compared to the water exchange rate constant of 6.6 × 10⁻⁶ (expressed in M⁻¹ sec⁻¹). Melson and Wilkins¹¹⁹ have shown that the second order rate constants for the formation of mono complexes of Ni(II) from Ni(OH₂)₆²⁺ with NH₃, N₂H₄, py, phen, dipy, terpy, etc. are all in the range of 2 × 10³ to 3 × 10³ M⁻¹ sec⁻¹ (at 25°C) which also suggests a dissociation mechanism as for the reaction of Co(NH₃)₅(OH₂)³⁺.

Formation of the monooxalato¹²⁰ and monoxalato¹²¹ complexes of Cr(III) from Cr(OH₂)₆³⁺ and the protonated forms of these ligands in acidic aqueous solution occur by a mechanism involving outer-sphere association (due to ion-pairing and hydrogen bonding interactions) between the reaction species and its transformation into the product by an essentially dissociative process in which loss of a water molecule from the hexaquo chromium (III) ion is only important in the transition state with no significant bond formation by the incoming ligand. A much lower ΔH[‡] value for the corresponding reaction with glycine, however, suggests significant associative character of the process¹²².

Formation of Cr(NH₃)₅X²⁺ complexes (X⁻ = chloride¹²³, thiocyanate¹²³, azide¹²⁴) have been studied and results are consistent with S_N1IP mechanism; Cr(OH)(OH₂)₅²⁺ also reacts with N₃⁻ by a similar process¹²⁴. In a study of the corresponding reaction of Cr(NH₃)₅(OH₂)³⁺ with acetate in HOAc NaOAc buffer media¹²⁵ both S_N1 and S_N1IP parallel reaction paths have been established. The formation of Co(NH₃)₅(N₃)²⁺ from Co(NH₃)₅(OH₂)³⁺ and azide (in HN₃-N₃⁻ buffer media as in our studies¹²⁴) also proceeds by an S_N1IP mechanism¹²⁶. A similar mechanism has also been suggested by us for the formation of Co(NH₃)₅(glycine)²⁺ from Co(NH₃)₅(OH₂)³⁺ and glycine in aqueous solution¹²⁷.

In the formation of Cr(Ox)₂(AA)⁻ from *cis*-Cr(Ox)₂(OH₂)₂ (AA = phen, dipy) results are consistent with a dissociative mechanism for the reagent independent path and an associative mechanism for the reagent dependent path¹²⁸. In the formation of Cr(BigH)₂(Ox)⁺ from *cis*-Cr(BigH)₂(OH₂)₂³⁺ S_N1IP mechanism has been established⁸⁹. Other formation reactions studied in our laboratory include formation of Cr(III)-EDTA complexes from several chelate complexes of Cr(III) and EDTA in alkaline media mentioned earlier¹¹¹ and the formation of Rh(III)-EDTA complex from RhCl₆³⁻ and EDTA in HCl media¹²⁹ all of which have interesting mechanistic features.

Mention has to be made in this connection about ligand substitution by redox mechanism. As early as 1927 Ray¹³⁰ reported the preparation of salts of the anion Co(CN)₅(S₂O₃)⁴⁻ by the action of CN⁻ on Co(NH₃)₅(S₂O₃)³⁺ which apparently involves replacement of NH₃ by CN⁻ in the Co(III) complex. Later on similar reactions with other complexes of the type Co(NH₃)₅X²⁺ (X⁻ = Cl⁻, Br⁻, I⁻, NO₂⁻, N₃⁻, NCS⁻, CN⁻ and OH⁻) have been carried out by others. But similar complexes where X = NH₃, OAc⁻, NO₃⁻, CO₃²⁻, SO₄²⁻ and PO₄³⁻ give rise to Co(CN)₅³⁻ as the sole product; while when X = F⁻ ca. 50% Co(CN)₅³⁻ and ca. 10% Co(CN)₄F³⁻ are formed. It is now known¹³¹⁻¹³³ that these reactions are catalyzed by traces of Co(II) present and actually involve electron transfer reactions proceeding by an *inner-sphere* (I.S.) mechanism in those cases where X is a ligand having good bridging properties leading to the formation of Co(CN)₅X³⁻; while when X is a ligand having poor or no bridging properties the reaction occurs by an *outer-sphere* (O.S.) mechanism forming Co(ON)₅³⁻ and both pathways are observed in the case of Co(NH₃)₅F²⁺. In CN⁻ medium Co(II) exists essentially as Co(CN)₅³⁻ with only traces of Co(CN)₄⁴⁻ due to the following equilibrium



the value of *K* is not known but an estimate is 10⁻¹ > *K* > 10⁻⁴. This equilibrium results in the following paths for reaction depending upon the nature of X as mentioned above :

the trigonal bipyramid is the preferred structure. Experimental evidences have been adduced in support of both square pyramid^{1,5,2} and trigonal bipyramid^{1,4,5 (b),1,5,3} intermediates for reactions in different Pt(II) systems.

It is significant that while PtCl_4^{2-} undergoes ligand exchange^{1,5,4} predominantly by Path I with Path II making a small contribution, the analogous reaction of AuCl_4^- , which is iso-electronic with PtCl_4^{2-} , is ca. 200 times faster (at 25°C) and Path II accounts for a larger fraction of the total exchange^{1,5,5} in the case of AuCl_4^- . This difference in behaviour is evidently due to a lower overall negative charge in AuCl_4^- compared to that in PtCl_4^{2-} . But the order of reactivities of different nucleophiles towards Au(III) substrate is comparable to that for Pt(II)^{1,5,6}. Thus, the behaviour of the complexes of Au(III) is comparable to those of Pt(II) but bond-making is more significant than bond-breaking in the case of Au(III) so that rate increases significantly in this case which increases in the overall positive charge of the complex and Au(III) complexes react much faster than those of Pt(II).

Kinetic data have been furnished^{1,5,7} to indicate that *trans-effect* which is so pronounced in the case of reactions of complexes of Pt(II) is absent in the case of complexes of Pd(II). Polarographic data^{1,5,8} indicate that the thermodynamic stability order is *trans* > *cis* both in the case of complexes of Pt(II) and Pd(II). Hence, the observed^{1,5,7} reactivity order *trans* > *cis* for Pt(II) and *cis* > *trans* for Pd(II) are purely kinetic characteristics of these systems. It has indeed been suggested^{1,4,4(b)} that *trans-effect* should be much less significant in complexes of Pd(II).

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