

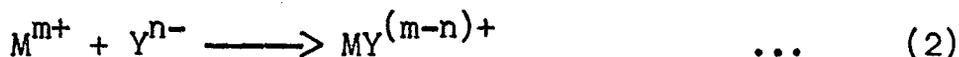
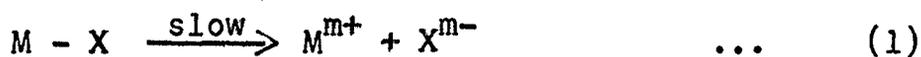
GENERAL INTRODUCTION

The experiments on replacement of one ligand by another in inorganic complexes was initiated by Alfred Werner¹ but the widespread interest in this field was shown by chemists only after the first review on ligand substitution dynamics by Taube² appeared in 1952. Now the study has gained considerable momentum, but many of the kinetic problems have been raised by these studies and much work has yet to be done to reconcile all the facts on a sound theoretical basis. Several recent reviews³⁻¹⁴ in this field have recorded the progress achieved so far.

Reaction of inorganic complexes can be broadly subdivided into three categories (1) Substitution reactions (2) Isomerization and racemization reactions which constitute a special type of substitution reactions and (2) Electron transfer or oxidation reduction reactions. Since the present work is related to substitution reactions, brief comments on certain aspects of substitution reactions will be made in this introductory chapter.

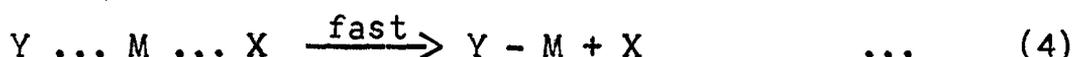
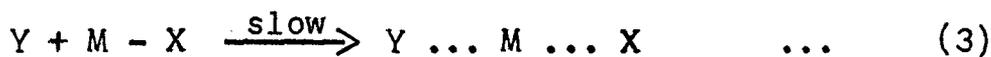
Substitution reactions involve the replacement of one ligand by another or one metal ion by another in a complex i.e. a bond is to be broken and a bond to be made. Using the terminology developed by Hughes and Ingold¹⁵ in describing organic reactions, we can call the above two groups of reactions as S_N (substitution nucleophilic) and S_E (substitution electrophilic). A nucleophilic reagent (ligand) donates electron to an electrophilic reagent (Central metal ion) in a complex which accepts it. Again an S_N reaction may be unimolecular (S_{N1}) or bimolecular (S_{N2}) depending on whether the transition state in the rate determining step involves one or two reacting chemical entities.

An S_{N1} reaction goes by a two step mechanism, a slow unimolecular heterolytic dissociation being the rate determining step



Here the slow bond breaking step 1 is followed by a rapid coordination step 2 and the coordination number of both the metal ion and ligand decreases by one in the rate determining step.

An S_N2 reaction involves a bimolecular rate determining step (3, below) followed by a fast bond breaking step (4, below) the coordination number of the metal ion increases by one in the transition state.



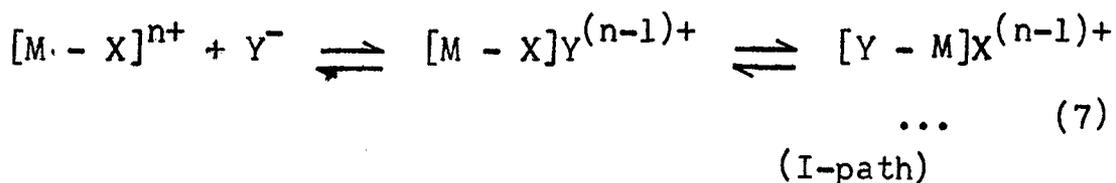
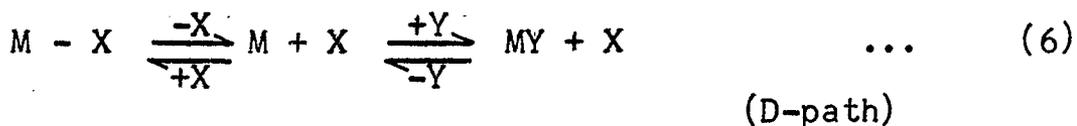
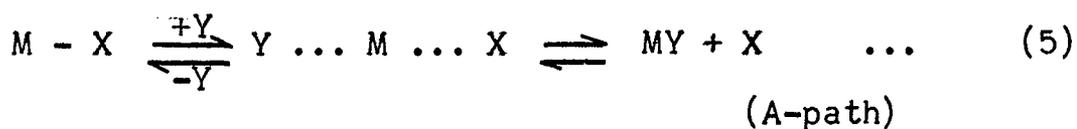
It is not correct to assume that a bimolecular reaction will always show second order kinetics and a unimolecular reaction a first order kinetics¹⁶. However, depending on the relative concentrations, the experimental conditions and the complexities of the overall reaction, different results may be obtained. The observed kinetics of a substitution reaction rarely gives the mechanism unambiguously¹⁷. Thus in order to make a choice between alternative mechanisms, many other factors viz. activation energetics, effect of charge and size of entering and leaving groups, oxidation state of the central metal ion and overall charge of the complex, the effect of ionic strength etc. should be examined. However, detection of an intermediate of reduced coordination number or an intermediate of increased coordination number by some means may be regarded as the best diagnosis of S_N1 or S_N2 mechanism.

Between these two extremes there may be borderline cases where bond making and bond breaking both are important, but to a different degree. For this reason it has been suggested to classify nucleophilic substitution reactions into four categories : S_N1 (Lim), where there is definite evidence for the intermediate of reduced coordination number in the rate determining step; S_N1 , where such definite evidences can not be presented; but which otherwise satisfies the requirements of a dissociation mechanism; S_N2 (Lim) where evidence for the intermediate of increased coordination number exists; and S_N2 , where the rate step involves bond breaking in $M - X$ and bond making in $M - Y$ equally.

Langford and Strengle⁹ tried to designate the substitution reactions according to the mode of activation. According to them substitution reactions involve two modes of activation; in the a-mode, transition state involves partial formation of a new bond with the incoming ligand (reaction 5, below) which helps the breaking of the $M - X$ bond while in d-mode there is no selective assistance by bond formation within the transition state (reaction 6, below). In the a-mode of activation a variation in the rate with the variation in entering ligand should be

observed, since covalence is presumably selective. In the d-mode of activation the rate should be effectively independent of the nature of the entering ligand.

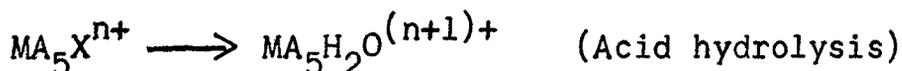
Three different pathways have been suggested for substitution reactions viz. two step associative path (A-path) two step dissociative path (D-path) and a two step interchange path (I-path) in which an ionpair $[M - X]Y$ is formed as an intermediate in a fast step and the ionpair suffers a slow innersphere outersphere ligand interchange.



The D-path and A-path involve d-mode and a-mode of activation respectively. The interchange of ligands between the solvation shell and the co-ordination shell in I-path may occur by either d-mode of activation (Id) or a-mode of activation (Ia). To an approximation, the four stoichiometric path ways D, A, Id and Ia may be considered as the same as S_N1 (Lim), S_N2 (Lim), S_N1 and S_N2 respectively.

Substitution reaction have been subdivided in the following heads:(a)

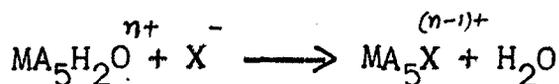
(a) Acid hydrolysis - The replacement of a ligand within a complex by a solvent water molecule is known as acid hydrolysis. The name acid hydrolysis comes from the fact that this reaction often predominates between pH 0 to 3.



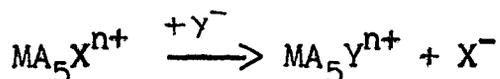
(b) Base hydrolysis - Base hydrolysis will imply replacement of X by hydroxide ion.



(c) Anation reaction - The replacement of coordinated water molecules in a complex by anionic ligands is often called anation reaction.

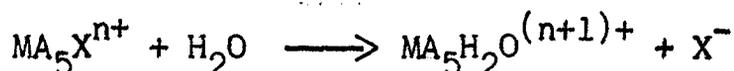


(d) Substitution reaction (anion-by-anion) - The replacement of an anionic ligand by another anionic ligand is called anion-by-anion substitution reaction.



(a) Acid hydrolysis :

In acid solution, $\text{pH} < 3$ (or $\text{pH} > 4$ in some cases) the substitution may be written as



where X in MA_5X^{n+} is replaced by H_2O . Since the reaction carried out in aqueous solution and the concentration of the ligand (solvent) is constant during the reaction, the rate is dependent only on the concentration of the complex and is first order or pseudo first order. This observation furnishes no information as to the role played by the water and does not tell anything about the molecularity of these reactions. Nevertheless the way in which rate constant is affected by various changes in the nature of the complex ion is expected to give us information about the mechanism.

It is found that increase in positive charge of the complex results in a remarkable decrease in the rate of acid hydrolysis¹⁸ indicating that bond breaking is of primary importance, since separation of negatively charged ligand is more difficult, the greater is the remaining charge of the complex in the transition state. However, such a decrease in the rate due to increased charge of the complex does not totally exclude solvent assistance,

since interaction of the charge of the complex with negatively charged ion always supersedes weak interaction with the dipole of water, and as such a decrease in rate with increase in positive charge of the complex should occur no matter whether there is any solvent assistance or not. 24

The decrease in rate with increase of chelation¹⁸ has been explained on the basis of solvation theory, which argues that increase in size of the complex accompanying chelation results in less stabilization of the transition state by solvation. This again does not exclude any bimolecular participation of water, since bond formation with water may take place in the transition state, side by side with solvation. All that one can suggest is the importance of bond-breaking in the transition state.

In complexes of the type $\text{trans-Co}(\text{AA})_2\text{Cl}_2^{1+}$ (AA = C- or N- alkyl substituted ethylenediamines) the rate of acid hydrolysis for the first chloride ion increases as the number or size of the C- or N- alkyl groups increases except when the alkyl group is a single methyl radical attached to nitrogen. This is strongly suggestive of a dissociation mechanism; when steric strain is relieved by expulsion of one ligand from the complex, the five coordinated intermediate is thereby stabilised. The solvation effect is much less than the steric strain effect

in these cases. This evidence highly disfavors an S_N2 mechanism which requires accommodation of the seventh ligand in these sterically crowded complexes¹⁹.

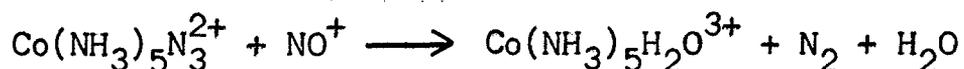
It has been shown²⁰ that influence of inductive effects on the rate is quite small in octahedral substitution and as such the increase in rate cannot be accounted for by increase of inductive effect through alkyl substitution.

Tobe and his coworkers²¹⁻²⁴ studied the rate of acid hydrolysis of cis- and trans-Coen₂LCl⁺ⁿ as function of varying tendency of L to donate electron to or accept electrons from the cobalt atom. It was found that as L was varied in the sequence L = OH⁻, N₃⁻, Cl⁻, NCS⁻, NH₃, H₂O, CN⁻ and NO₂⁻ of decreasing electron pair donor ability or increasing electron pair acceptor ability through metal to ligand π -bonding, the rate first falls, reaches a minimum and then again shows a rise with a maximum at NO₂⁻. It has been argued that π -acceptor ligands like NO₂⁻ and CN⁻ ions withdraw t_{2g} electrons from cobalt, by π -bonding, resulting in reduced electron density at the reaction site, thus facilitating at least some bond formation with water in the transition state by S_N2 mechanism and the rate increases as the π -electron accepting ability of L increases. Electron donating ligands like OH⁻, N₃⁻ etc. increases electron density around cobalt thus facilitating

the rate of dissociation of chloride ion in an S_N1 mechanism.

Thus a duality of mechanism is observed in aquation of cobaltamine complexes and the active mechanism would depend on the nature of the non-participating ligands.

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 ion in water enriched in ^{18}O , the product had the same $^{16}\text{O}/^{18}\text{O}$ ratio when Hg^{2+} was used to withdraw $\text{X}(\text{Cl}^-, \text{Br}^-, \text{I}^-)$ 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. Dolbear and Taube²⁶ showed that for a variety of leaving groups (L) from $\text{Co}(\text{NH}_3)_5\text{L}^{n+}$ the acid hydrolysis reactions are also consistent with the reaction proceeding through five coordinated intermediate by studying the isotope fractionation factor. Haim and Taube²⁷ studied oxidation induced aquation reaction.



in presence of added anions $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{SO}_4^=, \text{NO}_3^-, \text{SCN}^-$ and H_2PO_4^- . It was found that $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ complexes are also formed in addition to $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ suggesting formation of a five coordinated intermediate $\text{Co}(\text{NH}_3)_5^{3+}$

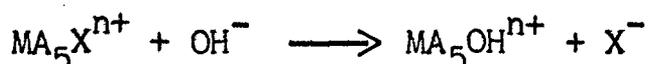
and subsequent reaction of this intermediate with H_2O and X^- . Further studies²⁸⁻³¹ of Hg^{2+} and NO^+ induced aquations of cis- and trans- $Coen_2Cl_2^+$, $Coen_2(N_3)_2^+$, $Coen_2N_3(H_2O)^{2+}$, $Coen_2H_2OC1^{2+}$, $Coen_2H_2OBr^{2+}$, $Coen_2ClBr^+$ and trans- $Coen_2ClN_3^+$ ions reveal that the ratio cis- and trans- products is independent of the leaving group giving a good evidence for five coordinated trigonal bipyramid intermediate.

A recent study of aquation³² of $Coen_2LC1^{2+}$ (L = aniline or p-toluidine) in mixed aqueous solvents shows that the rates are proportional to the concentration of water suggesting a bimolecular mechanism, since the rate differ much in solvents of identical dielectric constants, the possibility of S_N1 mechanism is greatly diminished.

It will thus be seen that the acid hydrolysis reactions of six-coordinated Co(III) complex do not follow S_N1 mechanism in each everycase, though evidences for S_N1 mechanism for such reactions have been found in a large majority of cases. The actual mechanism that is followed in a particular case is determined by the nature of the entering ligand and of ligands already present in the complex and the reaction conditions.

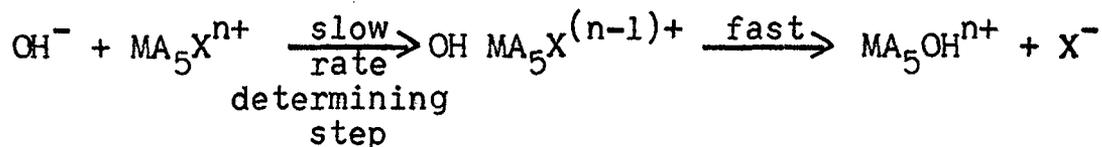
(b) Base hydrolysis :

The replacement of anionic ligand by hydroxide ion is called base hydrolysis.



Compared to all other nucleophiles hydroxide ion falls into a special category. Vary low concentration of hydroxide ion has an appreciable influence on the rate of release of halide ion and other labile ligands from nitrogen and water linked complexes of cobalt(III).

In all instances³³ in which a reaction with hydroxide ion can be detected, the reaction have been found to second order over all, first order in the complex and first order in OH^- ,



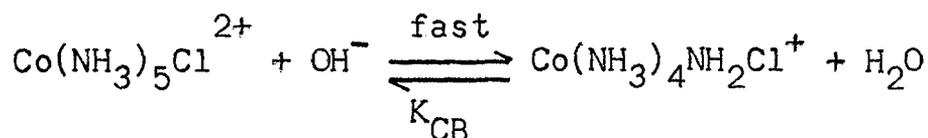
that is the formation of the M-OH bond may be important in the transition state of the rate determining step before the rupture of the M-X bond.

If we increase the chelation that is crowding in the complex³⁴, maintaining the leaving group fixed, theoretically it seems that rate should decrease because the crowding will hinder the formation of the seven coordinated intermediate.

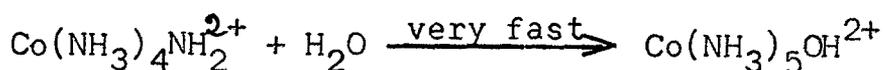
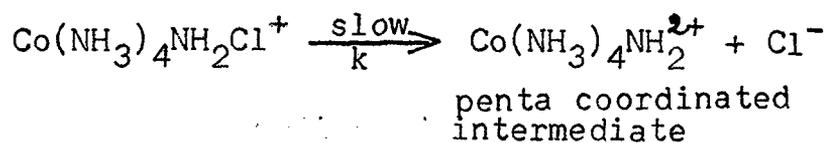
But experimental results show that increasing in chelation usually causes an increase in base hydrolysis rates. These observations cannot be explained by S_N2 mechanism.

A brilliant suggestion by Garrick who was inspired by the earlier work of Bornsted³⁵ opened up the door of explanation of such unexpected results on the basis of S_N1CB (Substitution Nucleophilic Unimolecular Conjugate Base) mechanism.

In the Garrick³⁶ mechanism, the ammine complex first forms conjugate base in small concentration in a rapid acid base equilibrium step.



The conjugate base then dissociate unimolecularly in a rate determining slow step to a penta coordinated intermediate. This penta coordinated intermediate immediately captures an aquo ligand forming the hydroxo species in a very fast step.



The rate equation for such a mechanism can be written as follows:

$$\begin{aligned} \text{Rate} &= k[\text{conjugate base}] \\ &= k K_{\text{CB}} [\text{C}][\text{OH}^-] \end{aligned}$$

Since $k_{\text{CB}} = \frac{[\text{CB}]}{[\text{C}][\text{OH}^-]}$ where C = complex and CB = conjugate base,

$$\begin{aligned} \text{Rate} &= k \cdot \frac{[\text{CB}][\text{C}][\text{OH}^-]}{[\text{C}][\text{OH}^-]} \\ &= \frac{k \cdot K_a [\text{C}]}{[\text{H}^+]} \quad \text{since } K_a = \frac{[\text{CB}][\text{H}^+]}{[\text{C}]} \\ &= \frac{k \cdot K_a [\text{C}][\text{OH}^-]}{K_w} \quad \text{since } K_w = [\text{H}^+].[\text{OH}^-] \end{aligned}$$

From this equation it can be seen that the observed second order rate constant for base hydrolysis equal to $k \cdot K_a / K_w$ though the reaction is actually dissociative.

The increased rate of base hydrolysis with increased chelation are also explained on the basis of $S_N1\text{CB}$ mechanism. The increased rate is due to the increasing in acid strength of the complexes with increasing chelation, that is K_a in the rate equation increases with chelation.

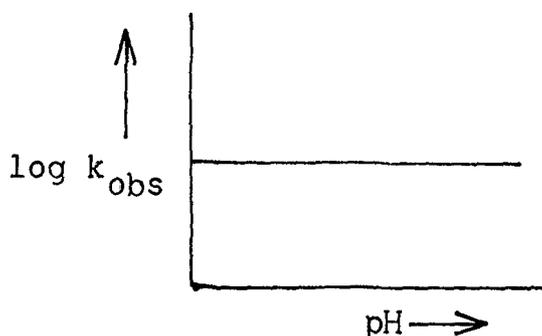
Increasing in C-alkyl substitution³⁷ in ethylenediamine of trans-[Coen₂Cl₂]¹⁺ the rate of base hydrolysis decreases due to reduction of the acidity of the complex by an inductive effect.

With increasing N-alkyl substitution³⁷ in ethylenediamine of trans-[Coen₂Cl₂]⁺ the rate of base hydrolysis increases due to further increase in the acidity of the complex.

However in many cases base hydrolysis data can be explained almost equally well by S_N1 CB and S_N2 mechanism and sometimes it becomes difficult to make a choice between these two alternatives and there are also cases in which S_N1 CB mechanism can be assigned with some definiteness thus establishing a dissociative mechanism. Thus in complexes having no acidic proton like Co(CN)₅Br³⁻ or Co(CN)₅I³⁻ undergo base hydrolysis³⁸ at first order rate independent of hydroxide ion concentration and as such these reactions are S_N1 and not S_N1 CB. As in these cases of complexes with high negative charge the failure to react with hydroxide ion may be due to electrostatic repulsion of [OH⁻] ion with the highly negative complex and as a result the S_N1 path for the reaction is favoured.

Very convincing arguments in favour of S_N1 mechanism of base hydrolysis are those of the hydrolysis of positively charged trans-dichlorotetrapyridine³⁹ series of

complex ions and of the $\text{cis-}[\text{Co}(\text{dipy})_2(\text{OAc})_2]^{1+40}$ ion which do not have acidic proton. The evidence that hydroxide ion do not play any role in the slow dissociation steps of the complexes to yield penta-coordinate intermediates, as in the case of S_N1 CB mechanism, is that the reaction are independent of pH. In that case the plot of $\log k_{\text{obs}}$ vs pH gives a straight line parallel to pH axes.



In the case of S_N1 CB mechanism

$$k_{\text{obs}} = \frac{k \cdot K_a [\text{OH}^-]}{K_w}$$

$$\text{or } \log k_{\text{obs}} = \log \text{const.} + \text{pH}$$

Therefore the plot of $\log k_{\text{obs}}$ vs pH should yield a straight line with slope = 1.0, this is the most characteristic test by which an S_N1 CB reaction can be distinguished from a pure S_N1 reaction. But this test cannot distinguish between S_N1 CB reactions and S_N2 reactions involving $[\text{OH}^-]$; for, the rate law of an S_N2 reaction involving $[\text{OH}^-]$ is

$$\text{rate} = k.[C][OH^-] = \frac{k.K_w.[C]}{[H^+]}$$

$$\therefore k_{\text{obs}} = \frac{k.K_w}{[H^+]} \text{ and } \log k_{\text{obs}} = \log \text{const.} + \text{pH}$$

Hence in the case of a reaction following S_N2 reaction too the slope of $\log k_{\text{obs}}$ vs pH straight line is + 1.

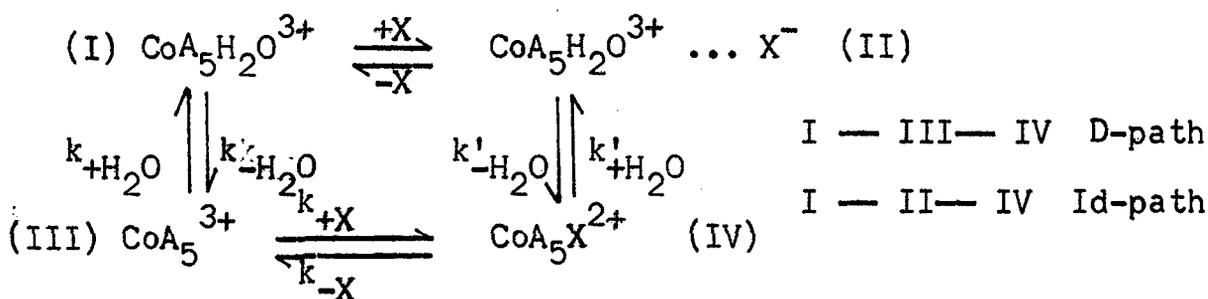
(c) Anation reaction :

The reverse of acid hydrolysis reaction i.e. the replacement of coordinated water molecules in a complex by anionic ligands is often called 'anation reaction' and can be represented as



Many anation reactions show an increase in rate with the concentration of the entering ligand^{41,42} and often attains the same limiting rate at high concentration, irrespective of the nature of the ligand. This suggests that in these reactions, there is no selective assistance from incoming ligand and the mechanism is presumably dissociative.

Two stoichiometric path ways for such anation reactions appear feasible and the two can possibly be distinguished.



Evidently, both the D-path and the Id-path should show reagent dependence and under certain restricted conditions second order kinetics is expected. In octahedral anation reactions evidences in favour of the dissociative interchange mechanism advocated by Langford and Tobe are more common, compared to the D-path, which is essentially S_N1 (Lim) mechanism.

In D-path a limiting rate of anion entry, if observable, at high anion concentration is expected to be independent of the nature of the anion and should be equal to the water exchange rate of species (I).

The equilibrium constant for anation (D-path) would be

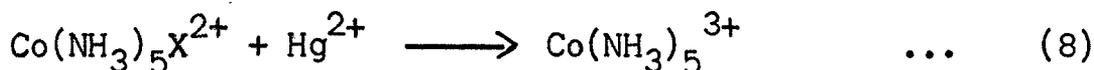
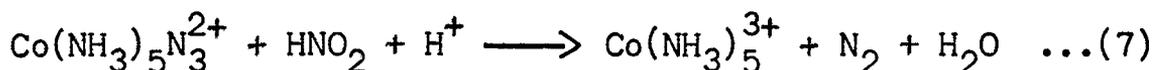
$$K = \frac{k_{-H_2O} \cdot k_{+X}}{k_{+H_2O} \cdot k_{-X}}$$

A knowledge of the rate of water exchange k_{-H_2O} of $\text{CoA}_5\text{H}_2\text{O}^{3+}$ and the rate of acid hydrolysis (k_{-X}) of $\text{CoA}_5\text{X}^{2+}$ (these are known in number of cases) gives the ratio

$\frac{k_{+X}}{k_{+H_2O}}$, the competition ratio for the intermediate CoA_5^{3+} .

A number of these competition ratios were computed by Haim and Taube⁴³, including the case $X = SCN^-$.

The factor $\frac{k_{+X}}{k_{+H_2O}}$ could be measured directly by generating the species CoA_5^{3+} in different ways in the presence of X^- , e.g.



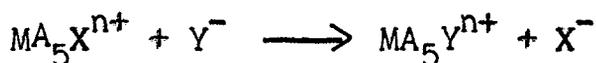
The ratio of subsequent products $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5X^{2+}$ would give the required ratio of $\frac{k_{+X}}{k_{+H_2O}}$, after allowing for the concentration of X^- . In a study of reactions (7) and (8) values of $\frac{k_{+X}}{k_{+H_2O}}$ were found⁴³ which agreed in some cases with those predicted from the equilibrium constant. Pearson and Moore⁴⁴ generated the intermediate by hydrolysis of the labile nitrate and bromo-pentaammines of Co(III) in presence of 0.5 M NCS^- , then they are converted directly to $Co(NH_3)_5H_2O^{3+}$ to the extent of more than 98%. No $Co(NH_3)_5NCS^{2+}$ can be detected as an intermediate product. So the basic assumption of D-path is incorrect in these cases.

The Id-path also predicts a limiting anation rate corresponding to complete formation of ion-pair at high anion concentration and this rate should be lower than the water exchange rate of the ion pair (species II) by an appropriate statistical factor arising out of greater statistical advantage of a water molecule to be suitably oriented at the reaction site. Thus, the rates of formation of $\text{Co}(\text{NH}_3)_5\text{X}$ from $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O} \dots \text{X}$ have been reported^{45,46}, for $\text{X} = \text{SO}_4^{=}$, Cl^- , SCN^- and H_2PO_4^- ; these are lower than the water exchange rates of the ionpairs by factors of 0.24, 0.21, 0.16 and 0.13 respectively. Murray and Barraclough⁴⁷ found the rate of sulfate anation in the pair $\text{cis}[\text{Coen}_2(\text{H}_2\text{O})_2]^{3+} \dots \text{SO}_4^{=}$ to be 0.25 times the water exchange rate of the free ion. Duffy and Early⁴⁸ reported the rate of entry of Cl^- and SCN^- into $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ as compared to water exchange rate and it was 5% of the water exchange rate. Brown and Harris⁴⁹ showed that anation of $\text{Coen}_2(\text{H}_2\text{O})_2^{3+}$ with oxalate proceed by Id mechanism and the extrapolated rate at infinite anion concentration is about one fourth the water exchange rate of the free ion. But Ray and Siddhanta⁵⁰ has explained the kinetics of the same reaction (i.e. that between $[\text{Coen}_2\text{Cl}_2]^+$ and oxalate on the basis of a purely dissociative mechanism.

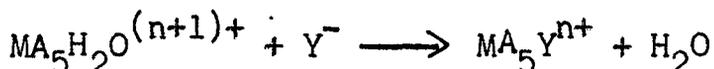
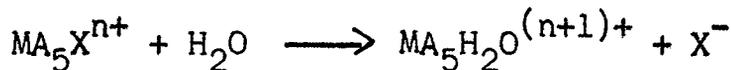
(d) Substitution reaction (Anion-by-Anion) :

The replacement of an anionic ligand (Anion) within a complex by another anionic ligand is called 'anion-by-anion substitution reaction'.

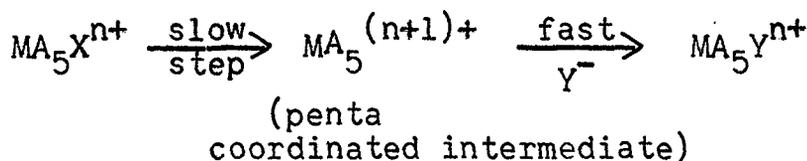
The general form of the reaction is as follows :



Many reaction of the above type in which Y is not hydroxide ion, the reaction proceed through the intermediate formation of aquo complex i.e.



But there are a large number of cases where MA_5X^{n+} (M = Co(III)) dissociates in a slow step to give the penta coordinated intermediate $MA_5^{(n+1)+}$ which then captures Y^- in a fast step



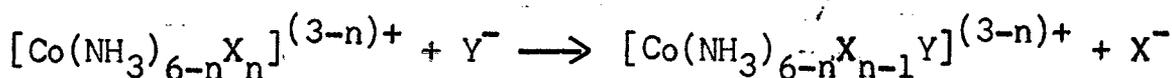
Since the order of reaction in which X^- is liberated is in both cases zero with respect to Y^- , there is no way to test the effect of the nature of Y^- on the rates.

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Ardon⁵¹ studied the substitution reactions of Iodo-pentaaquo chromium(III) ion by Br^- and Cl^- and found that reaction proceeds without intermediate formation of hexa-aquo ion. On the contrary bromopentaaquo chromium(III) ion is formed along with hexaaquo chromium(III) ion at a concentration ratio of 0.127 (in 1 M HBr). Similar results were obtained in the presence of Cl^- . The results were interpreted by $\text{S}_{\text{N}}1$ mechanism.

Haim and Wilmarth⁵² have shown that the substitution of N_3^- by NCS^- in $[\text{Co}(\text{CN})_5\text{N}_3]^{3-}$ does not proceed with intermediate formation of $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$, water and thiocyanate compete for the same intermediate $[\text{Co}(\text{CN})_5]^{2-}$, which was formed by the loss of azide from the reactant. Haim and Taube⁵² found evidence of formation of the intermediate $[\text{Co}(\text{NH}_3)_5]^{3+}$ in substitution reaction of cobalt amines. Ray and Siddhanta⁵⁰ reported that substitution of Cl^- in $\text{cis}-[\text{Coen}_2\text{Cl}_2]^+$ by oxalate ion proceeds through the formation of pentacoordinated intermediate, which is then competitively captured by both water and oxalate ion. Ghoshal and Siddhanta⁵³ also reported that substitution of Cl^- in $\text{cis}-[\text{Coen}_2\text{Cl}_2]\text{Cl}$ by p-hydroxybenzoic acid proceed through two step, the first step being the formation of the pentacoordinated intermediate $[\text{Coen}_2\text{Cl}]^{2+}$ and the second step being the competitive capture of H_2O and benzoate ion by this pentacoordinated intermediate.

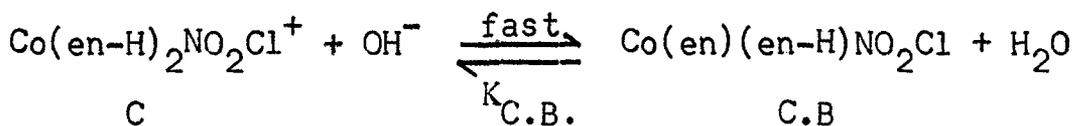
The conjugate base mechanism often operates in anion-anion substitution of the type



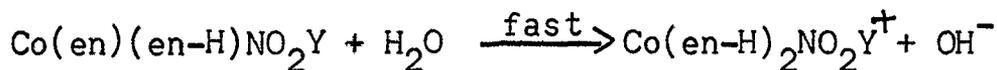
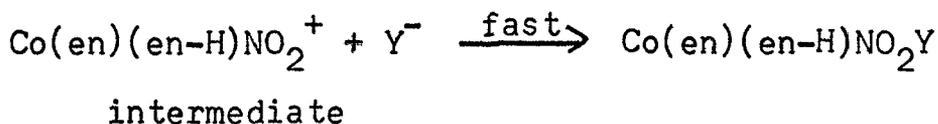
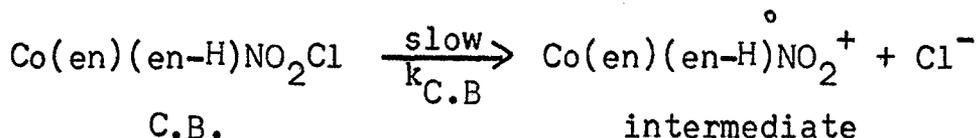
$$n = 1 \text{ or } 2$$

but such reactions are OH^- catalysed reaction are not base hydrolysis reaction. This type of reaction may also operate in anation reaction.

It has been observed that in dry dimethyl sulphoxide medium the complexes of the type $\text{trans-}[\text{Coen}_2\text{NO}_2\text{Cl}]^{+54}$ reacts with Y^- ($\text{Y}^- = \text{NO}_2^-, \text{CNS}^-, \text{N}_3^-$ or OH^-) to form $[\text{Coen}_2\text{NO}_2\text{Y}]^+$ with equal rates in every case at a particular pH. This might suggest that each reaction follows $\text{S}_{\text{N}}1$ path leading to the formation of a pentacoordinated intermediate with the release of Cl^- in the present complex at the same slow rate and the pentacoordinate intermediate captures Y^- in a very fast step. But on adding a certain amount of OH^- ions to the reaction medium in each, each of the reaction becomes faster to the same extent and all the reaction rates becomes the same again at the higher pH. This fact cannot be accounted if the mechanism were pure $\text{S}_{\text{N}}1$. $\text{S}_{\text{N}}1$ CB mechanism for each of the reaction has to be invoked for the correct explanation.



where en-H = $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ i.e. ethylenediamine



The OH^- ion used in the first step is regenerated in the last step, but through its influence, the reaction rate is increased. It is therefore OH^- ion catalysed anion by anion substitution reaction. Here the rate law is given by

$$\text{rate} = k_{\text{CB}}[\text{CB}] \quad (\text{second step})$$

But from the equilibrium in the first step, we have

$$K_{\text{CB}} = \frac{[\text{CB}]}{[\text{C}][\text{OH}^-]}$$

$$\therefore \text{rate} = k_{\text{CB}} \cdot K_{\text{CB}} [\text{C}][\text{OH}^-] = k_{\text{CB}} \cdot K_{\text{CB}} \cdot K_w [\text{C}] / [\text{H}^+]$$

Therefore

$$k_{\text{obs}} = k_{\text{CB}} \cdot K_{\text{CB}} \cdot K_w \cdot \frac{1}{[\text{H}^+]}$$

$$\text{Hence } \log k_{\text{obs}} = \log \text{const.} + \text{pH} .$$

Thus in an OH^- catalysed anion-by-anion substitution reaction, the plot of $\log k_{\text{obs}}$ vs pH is a straight line with slope +1 and this is the most characteristic test of an OH^- catalysed anion-by-anion substitution reaction.

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