CHEM3012 - Core Chemistry 3

Inorganic Reaction Mechanisms

4. Substitution reactions of octahedral complexes

The substitution of ligands in octahedral metal complexes is the most extensively mechanistically studied inorganic reaction. It is of fundamental importance, and a number of important observations and results are found. Substitution in octahedral systems was initially studied for classical coordination complexes in aqueous solutions. More recently some important observations have been made regarding the mechanism by which organometallic complexes under ligand substitution reactions. We will consider these organometallic complexes after a discussion of the aqueous reaction mechanisms.

The following three sections cover:
- Substitution reactions of classical octahedral complexes in general
- Points which are specific to Co(III), mainly since it is the most extensively investigated metal/oxidation state.
- Some octahedral organometallic substitution chemistry.

4.1. Substitution reactions of classical octahedral complexes in aqueous solutions

The most fundamental reaction to investigate is the reaction of the aquo ions $M(H_2O)_6^{n+}$. The reactions which are possible are substitution of water by water, and substitution of water by an anionic ligand, X^-. These apparently simple reactions <u>can</u> display all the possible mechanisms A, I or D. In fact I_a and I_d mechanisms predominate in octahedral systems, whilst D and A mechanisms are rare.

4.1.1. Eigen-Wilkins mechanism

For this, and other, work on mechanisms of reactions Eigen won the 1967 Nobel Prize with Norrish and Porter). Interchange reactions proceed via an initial pre-equilibrium leading to the formation of an encounter complex which then rearranges to give the products. The Eigen-Wilkins mechanism can be applied to all molecular reactions in solution that occur at rates less than the diffusion limit.

Unfortunately the rate expressions predicted by the Eigen-Wilkins mechanism can all reduce to the same expression under appropriate conditions, such as large concentrations of X, constant concentration of H_2O (a highly likely case) and small or large k_{-w}, k_x etc. In consequence the rate law is almost useless in determining the nature of the mechanism of substitution in octahedral complexes. The accumulated evidence suggests that for most octahedral complexes, the I_d mechanism operates. The rest of this section will present and discuss the evidence which confirms this conclusion.

4.1.2. Substitution reactions of aquo ions: Substitution of water by water

The factors which we can examine here are the following:

  (a) how the rate varies as a function of metal

  (b) size / charge considerations

  (c) LFSE (Ligand field stabilisation energy) factors

  (d) The mechanism

These factors can be examined by considering many different types of reaction, but the two that are the most widely studied are substitution of water by X (anation), and substitution of X by H_2O (hydrolysis)

Unfortunately these rate expressions can all reduce to the same expression, Rate = k_f[complex][X], under appropriate conditions of large [X], constant [H_2O], small or large k_{-w}, k_x etc.

The rate law is almost useless in determining the nature of the mechanism of substitution in octahedral complexes.
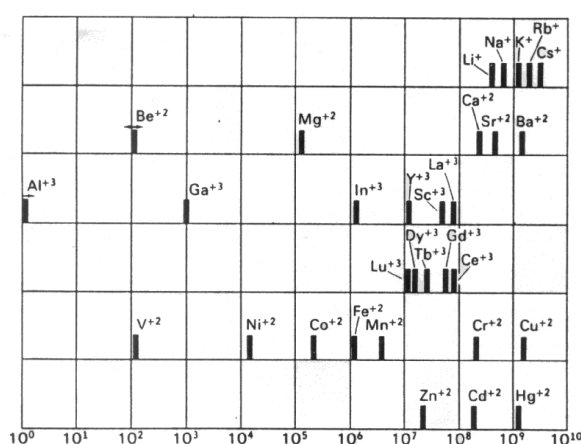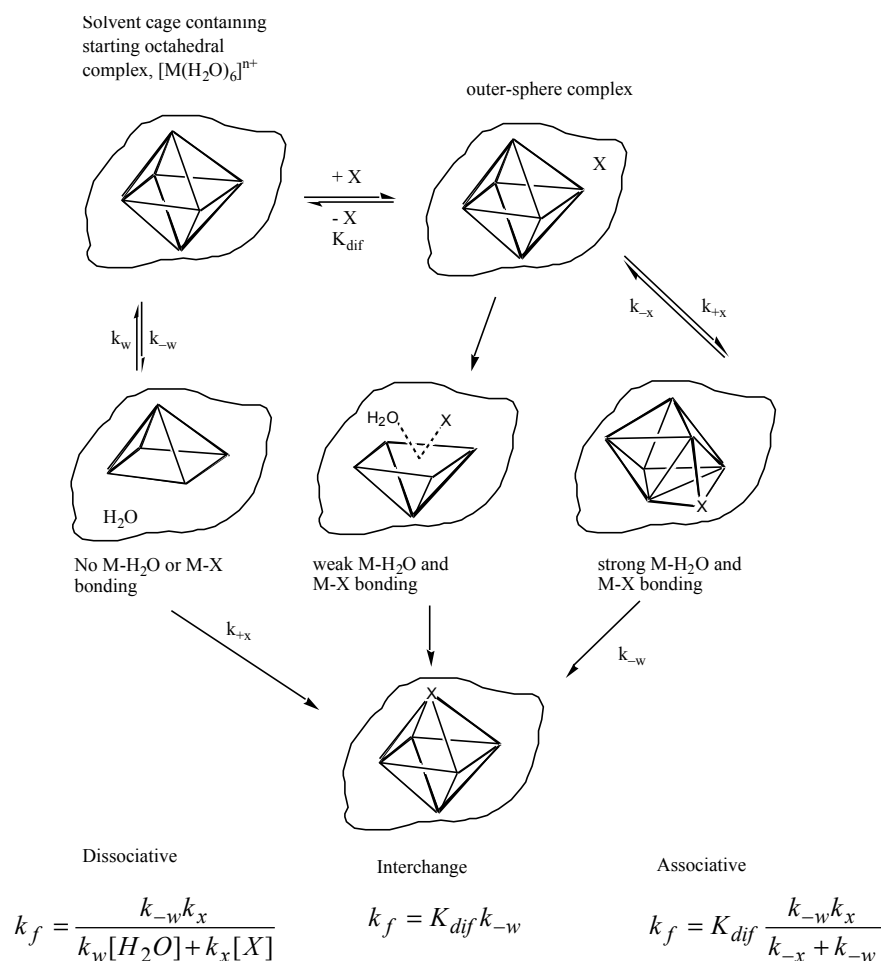
The accumulated evidence suggests that for most octahedral complexes, the I_d mechanism operates.

4.1.3. Substitution reactions of aquo ions: Substitution of water by water

$$M(H_2O)_6^{n+} + H_2O^* \rightleftharpoons M(H_2O)_5(H_2O^*)^{n+} + H_2O$$

The hydration number of most metals is 6 (the most notable exceptions are Be^{2+} and Ca^{2+} = 4 coordinate; lanthanides = higher). The process depicted in the equation above is the most fundamental ligand substitution process, namely

substitution of bound H_2O by solvent water. The kinetics of this reaction have been studied by a number of techniques including relaxation methods and NMR. Kinetic data are known for the vast majority of metal aquo ions, and the measured range of rates is vast, covering 18 orders of magnitude (figure). Substitution is fast for most metals, however as far as kinetic studies are concerned it is the slow ones which can be more useful.

$$k_f = \frac{k_{-w}k_x}{k_w[H_2O]+k_x[X]}$$

Dissociative

$$k_f = K_{dif}k_{-w}$$

Interchange

$$k_f = K_{dif}\frac{k_{-w}k_x}{k_{-x}+k_{-w}}$$

Associative

Rate constants (sec^{-1}) for the substitution of water molecules in $M(H_2O)_n^{x+}$ ions.

Taube provided the first classification of this data (1952) and he introduced two terms, labile and inert.

- Labile - react rapidly, within seconds
- Inert - react more slowly, minutes or longer for substitution

Further consideration of the data allows a classification of the metals into 4 classes

- Very fast, diffusion controlled rates ($> 10^8$ s^{-1}): Groups 1, 2 (except Be^{2+}, Mg^{2+}), Cd^{2+}, Hg^{2+}, Cr^{2+}, Cu^{2+}
- Moderately fast (10^4 to 10^8 s^{-1}): 1st row transition metals (except V^{2+}, Cr^{2+}, Cu^{2+}), Mg^{2+} and Ln^{3+}
- Slowish substitution $1 - 10^4$ s^{-1} Be^{2+}, Al^{3+}, V^{2+} and some Transition Metal^{3+}
- Very slow substitution (10^{-3} to 10^{-6} s^{-1}): Cr^{3+}, Co^{3+}, Rh^{3+}, Ir^{3+}, and $Pt^{2+.}$

4.1.4. Rationalisation of data

There are a number of factors which can account for the variation in the rate of water exchange and these are consdiered in turn.

4.1.4.(a). Variation of rate with metal charge and size

Size / charge ratio can account for the behaviour of all the non-transition metals. The M-OH$_2$ bond strength increases with increasing metal charge and M-OH$_2$ bond strength decreases as metal size increases. The ligand substitution rate is largest for large monovalent ions:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

$$\text{fastest } M^+ > M^{2+} > M^{3+} \text{ slowest}$$
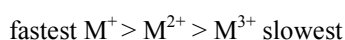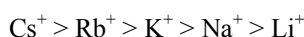
From these observations we can conclude that M-OH$_2$ bond breaking is of more importance than M-*OH$_2$ bond making in the transition state. This implies a dissociative mechanism (I_d or D). Recall that for a dissociative mechanism, bond breaking is important in the transition state, whilst for an associative mechanism bond making is important in the transition state.

4.1.4.(b). Variation of rate with d electron count

4.1.4.b.i Metals for which substitution is fast (Cu^{2+}, Cr^{2+}).

These d^9 and d^4 metals have active Jahn-Teller distortions. Recall the J-T theorem:- If the ground electronic configuration of a non-linear molecule is degenerate, the molecule will distort so as to remove the degeneracy and become more stable. Remember, the theorem only predicts a distortion, not the size and/or nature of the distortion. In the case of both Cu^{2+} and Cr^{2+} it turns out experimentally that the distortion is normally axial - resulting in longer bonds to two water molecules, which are held less strongly, and so are more readily substituted. The diagram is drawn for the d^9 configuration: The fast H$_2$O exchange reactions of Cu^{2+} and Cr^{2+} are suggestive of a dissociative mechanism (I_d).
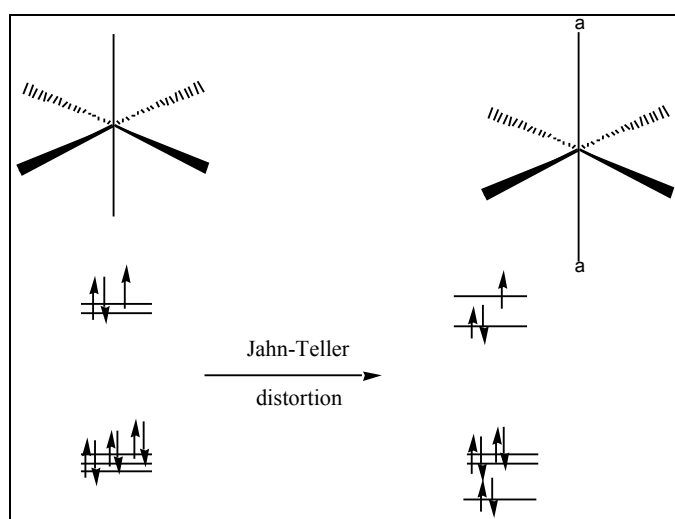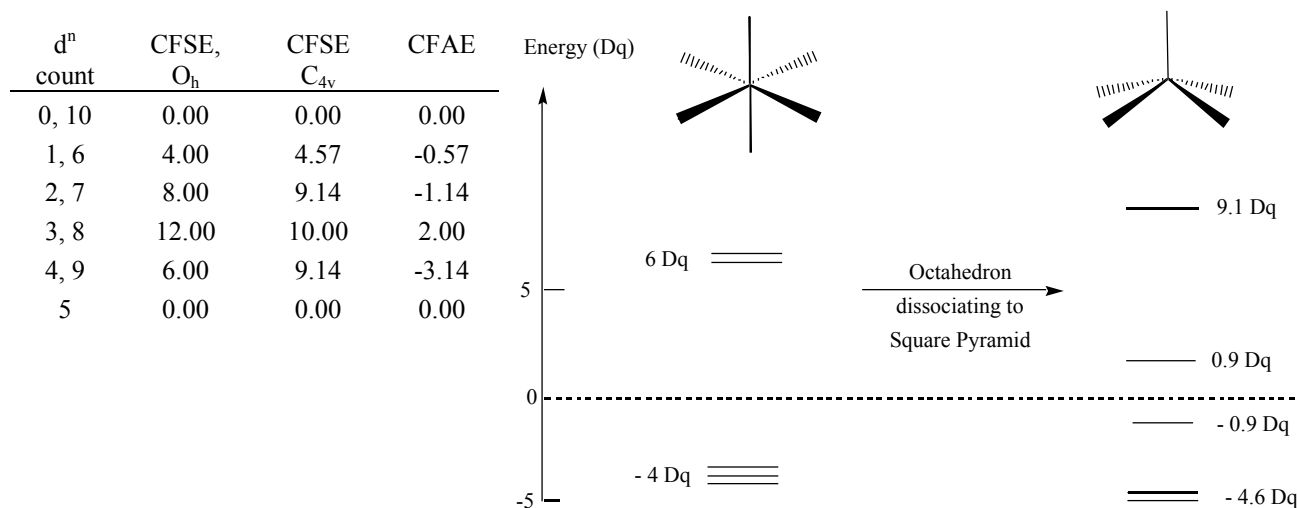

4.1.4.b.ii Metals other than Cu^{2+} and Cr^{2+}

The following interpretation is due to Basolo and Pearson (1967)

- Calculate CFSE for octahedron (ground state) and all possible transition state geometries.
- Only discussing HIGH SPIN complexes for the moment.
- Assume that magnitude of the crystal field parameter (Δ or Dq) is invariant of geometry and metal.
- Assume that the activation energy is mainly due to the d orbital energy change between ground and activated states.
- Calculate activation energies in terms of Dq units.

The figure below shows the crystal field splitting patterns for the octahedron (6 coordinate, point group O_h) and the

square based pyramid (5 coordinate, C_{4v}) geometries. The table shows the crystal field stabilisation energies (CFSE) obtained for each d^n configuration in each of these geometries. The difference between these two CFSE values is then the crystal field activation energy (CFAE), or the energy required for the octahedron to dissociate one ligand as it moves towards the transition state in a dissociative ligand substitution reaction.

d^n count	CFSE, O_h	CFSE C_{4v}	CFAE
0, 10	0.00	0.00	0.00
1, 6	4.00	4.57	-0.57
2, 7	8.00	9.14	-1.14
3, 8	12.00	10.00	2.00
4, 9	6.00	9.14	-3.14
5	0.00	0.00	0.00

The assumption is made that the activation energy for the ligand substitution process is made up of a number of factors, of which the crystal field contribution is just one. The other influences are assumed to be constant across the transition series, and hence the trend in the rates of ligand substitution of the transition metal aquo complexes can be interpreted on the basis of the CFAE (lower CFAE = faster rate).

The figure and table above only relate to a ligand substitution process that operates via a dissociate process (D or I_d) involving an intermediate (D) or transition state (I_d) of lower coordination number. A similar set of CFAE data can be derived for associative processes involving higher coordination number transition states or intermediates. The construction of such a table is left as an exercise for the student, as is the consideration of low spin complexes.

The calculations show that for a high spin O_h - C_{4v} dissociative ligand substitution the relative rates are predicted to be:

$(d^4, d^9) > (d^2, d^7) > (d^1, d^6) > (d^0, d^5, d^{10}) > (d^3, d^8)$

The table lists some experimental results:

complex	d count	rate (s^{-1})
$[V(H_2O)_6]^{2+}$	d^3	87
$[Cr(H_2O)_6]^{2+}$	d^4, hs	$> 10^8$
$[Mn(H_2O)_6]^{2+}$	d^5, hs	2.1×10^7
$[Fe(H_2O)_6]^{2+}$	d^6, hs	4.4×10^6
$[Co(H_2O)_6]^{2+}$	d^7, hs	3.2×10^6
$[Ni(H_2O)_6]^{2+}$	d^8	3.2×10^4
$[Cu(H_2O)_6]^{2+}$	d^9	$> 10^7$
$[Zn(H_2O)_6]^{2+}$	d^{10}	$> 10^7$

This theory has some successes:

- Correctly predicts that Ni(II) and V(II) should be slowest and that Cr(II) and Cu(II) should be the fastest.
- Substitution of d^3 should be slow and a more detailed consideration also predicts that the substitution of low spin d^6 should also be slow. The classic cases of these electronic configurations are Cr^{3+} and Co^{3+}.

There are some limitations to the theory

- Theory breaks down as far as the EXACT order of Co(II), Fe(II), Mn(II) and Zn(II) are concerned.
- Not good at predicting absolute magnitudes of rates / activation energies e.g., Ni(II) and V(II) are very different in rates (charge / size ratios ?)
- In the discussion above a dissociative mechanism has been assumed, and there is plenty of evidence that this is not valid. A consideration of dissociative AND associative mechanisms suggests that substitution via an octahedral wedge (7 coordinate) geometry (Associative A or I_a) is predicted by the theory to be faster for (d^1, d^6) and (d^3, d^8), whilst an associative process via a pentagonal pyramid (7 coordinate) is faster for (d^2, d^7)

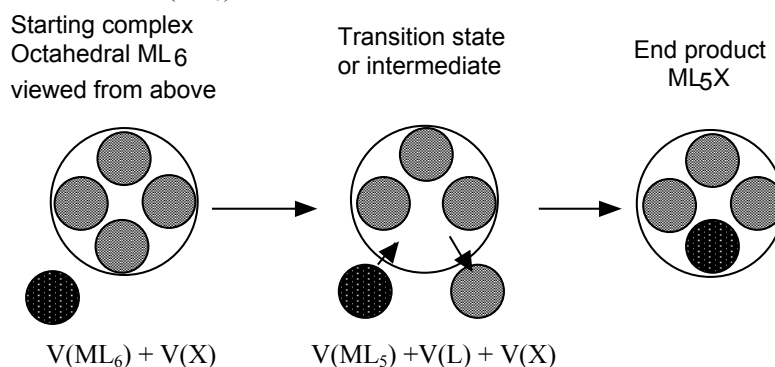- Many "improvements" to this theory have been proposed.

Crystal Field theory usefully predicts a qualitative order of which transition metal complexes should be inert or labile. However the theory is not very good when it attempts to judge any preference for dissociative or associative mechanisms.

4.1.4.(c). Volume of activation

It is necessary to use some other theory, or experimental data in order to conclusively decide whether substitution reactions of metal aquo cations proceed via associative or dissociative mechanisms. One of the most useful experimental techniques relates to the volume of activation. To introduce this for the ligand substitution reaction of a ML_6 complex, consider the volume of the complex at the transition state relative to the volume in the ground state in both associative and dissociative reaction mechanisms.

### 4.1.4.c.i ML_6 reacting with X by a dissociative mechanism.

The molar volume of ML_6 is $V(ML_6)$, the molar volume of X is $V(X)$, and the molar volume of the 5 coordinate transition state or intermediate is $V(ML_5)$

	Starting complex Octahedral ML_6 viewed from above	Transition state or intermediate	End product ML_5X
Vol:	$V(ML_6) + V(X)$	$V(ML_5) + V(L) + V(X)$	

Experimental data show that the volume swept out by ML_5 is almost as large as that of ML_6. Thus $V[Ni(NH_3)_6{}^{2+}] = 138$ $cm^3\ mol^{-1}$ and $V[Ni(NH_3)_5{}^{2+}] = 137.9\ cm^3\ mol^{-1}$

Thus, for a dissociative process the molar volume of the transition state is higher than that of ground state. The volume of activation ($\Delta V^{\ddagger}$, defined as the volume change between the ground state and the transition state or intermediate) is positive for a dissociative process, and has a magnitude almost as large as $V(L)$, the molar volume of the incoming ligand.

A consideration of all the possible mechanisms gives the following predictions of how $\Delta V^{\ddagger}$ will vary:

	D	I_d	I_a	A
$\dfrac{\Delta V^{\ddagger}}{V(L)} =$	~ +1	< +1	~0 >−1	−1
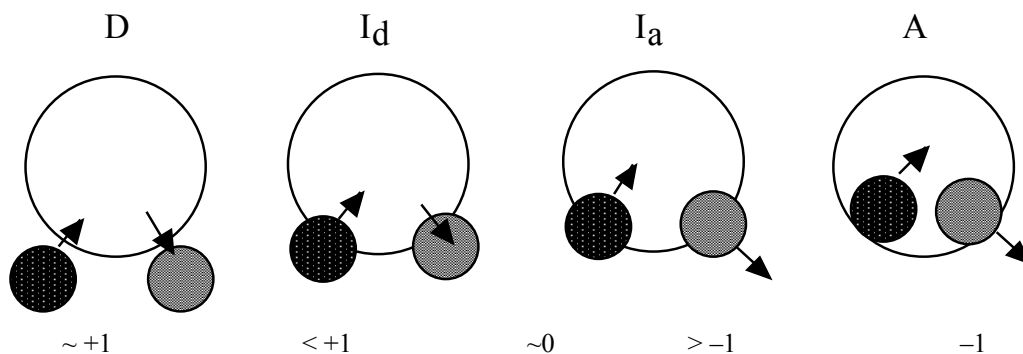
complex	d count	rate(s^{-1})	$\Delta V^{\ddagger}$	Mechanism
$[V(H_2O)_6]^{2+}$	d^3	87	-4.1	Ia
$[Cr(H_2O)_6]^{2+}$	d^4, hs	$>10^8$		
$[Mn(H_2O)_6]^{2+}$	d^5, hs	2.1×10^7	-5.4	Ia

|				
$[Fe(H_2O)_6]^{2+}$	d^6, hs	4.4×10^6	3.8	Id
$[Co(H_2O)_6]^{2+}$	d^7, hs	3.2×10^6	6.1	Id
$[Ni(H_2O)_6]^{2+}$	d^8	3.2×10^4	7.2	Id
$[Cu(H_2O)_6]^{2+}$	d^9	$>10^7$		
$[Zn(H_2O)_6]^{2+}$	d^{10}	$>10^7$		

The measurement of $\Delta V^{\ddagger}$ is potentially an easy experiment to perform. The van't Hoff equation, familiar from earlier lectures on thermodynamics, is

$$-\frac{\Delta V^{o}}{RT} = \left(\frac{\delta \ln K}{\delta P}\right)_T$$

and relates the variation of an equilibrium constant (K) with pressure to the specific volume change of the reaction (volume of reactants less volume of products). The kinetic equivalent relates the variation of rate constant (k) with pressure to the volume of activation, so that $\Delta V^{\ddagger}$ is given by measuring the variation of the rate constant with pressure at constant temperature by

$$-\frac{\Delta V^{\ddagger}}{RT} = \left(\frac{\delta \ln k}{\delta P}\right)_T$$

The figure shows the plots which have been obtained for some transition metal ions. The table above shows how the data correlate with d electron count.
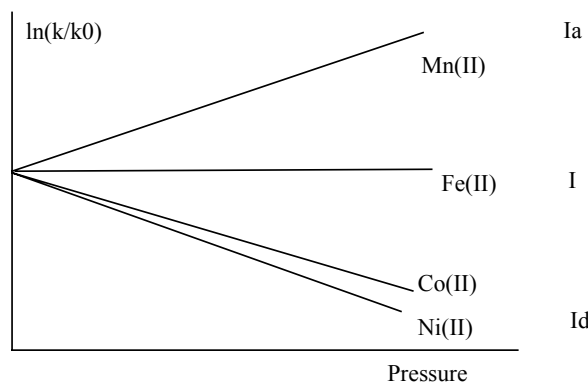

- Increasing the number of d electrons (especially in the t_{2g} set) disfavours associative pathway, since the approaching ligand comes along the three-fold axis of the octahedron, and the electrons of the incoming ligand interact with the t_{2g} electrons.
- The size of the cation decreases across the transition series

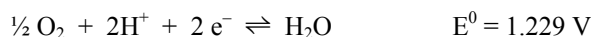### 4.1.5. Summary of observations to date on substitution reactions in octahedral complexes

- Many studies of substitution reactions of octahedral complexes provide evidence for I_d mechanisms.
- Some reactions can have I_a character especially for the larger metal ions (V^{2+}, 2nd and 3rd row d block metals).
- Larger metals facilitate the necessary higher coordination numbers for associative reactions.
- Exchange rates are slow for d^3, d^8 and low spin d^6.

4.2. Mechanisms of substitution reactions in Co(III) complexes

We will now discuss some detailed mechanistic points. Most of the studies which are now going to be discussed are based on d^3 and low spin d^6 complexes. The classic examples of these configurations are Cr^{3+} and Co^{3+}. Why have we not considered the rate of water exchange with $[Co(H_2O)_6]^{3+}$ according to the following reaction ?

$$Co(H_2O)_6^{3+} + H_2O^* \rightleftharpoons Co(H_2O)_5(H_2O^*)^{3+} + H_2O$$
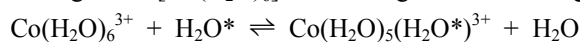
Co(III), d^6 low spin, octahedral, t_{2g}^6 configuration, maximum CFSE,

$$[Co(H_2O)_6]^{3+} + e^- \rightleftharpoons [Co(H_2O)_6]^{2+} \quad E^0 = 1.83 \text{ V}$$

$$\tfrac{1}{2} O_2 + 2H^+ + 2 e^- \rightleftharpoons H_2O \qquad E^0 = 1.229 \text{ V}$$

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \quad E^0 = 0.108 \text{ V}$$

Conclusion: Co(III) aquo complexes are highly oxidising.

Nitrogen donor ligands reduce the oxidising power and mean that a wide range of amine complexes are known. These N-donor complexes substitute slowly and provide a wealth of suitable compounds for more detailed study

4.2.1. Co(III) provides further evidence for I_d mechanisms

Leaving group effects are expected to be large in I_d mechanisms since $\Delta G^\ddagger$ is largely determined by breakage of the M-X bond. So vary the leaving group X. The most extensively studied systems are the forward (hydrolysis) and reverse (anation) of the following reaction:

$$[Co(NH_3)_5X]^{2+} + H_2O \underset{\text{anation}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} [Co(NH_3)_5(H_2O)]^{3+} + X^-$$
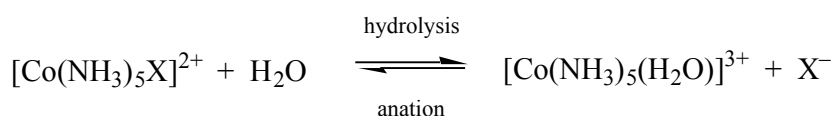
For this reaction it is possible to vary X (F^-, Cl^-, NO_3^-) and measure both the rate constant (k) and equilibrium constant (K).

The graph shows that there is a relationship between the logarithms of rate constant and equilibrium constant.

$$\log k = \log K + c$$

Since logarithms of rate constants and equilibrium constants are proportional to free energy changes, an alternative expression of this equation is

$$\Delta G^\ddagger = a \, \Delta G^\circ + b$$

This is known as a **Linear Free Energy Relationship**. There are many examples known of such relationships in many branches of physical chemistry. In this case the constant a = 1.00, although there exist LFER's with values of a that are non-unity.

- The observation that the reaction shows a LFER has some implications for the reaction mechanism.
- Changing the Co-X function has the same effect on the rate (k) as it has on the equilibrium constant (K).
- Changing the Co-X function has the same effect on activation free energy as on the overall free energy.
- Since the overall reaction will involve solvation of X-, this implies solvation of X- in the activated complex.
- This implies a Dissociative (Id) mechanism.

The observation of a LFER with unit slope implies that changing X has the same effect on $\Delta G^\ddagger$ for the conversion of M-X to the activated complex as it has on the ΔG° for the complete elimination of X-. The reaction profile shows the effect of changing the leaving group from X to X'.


Reaction coordinate
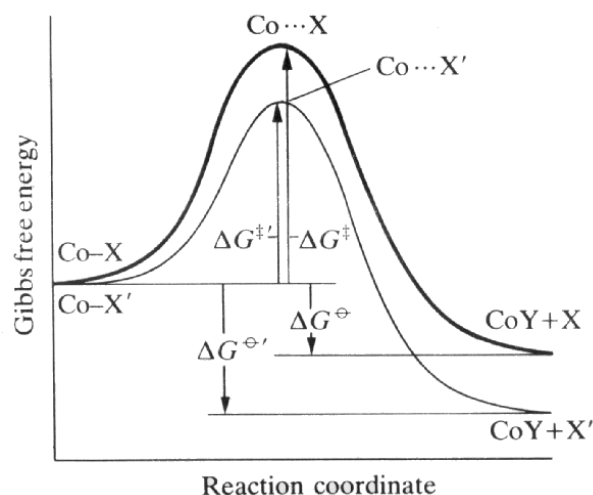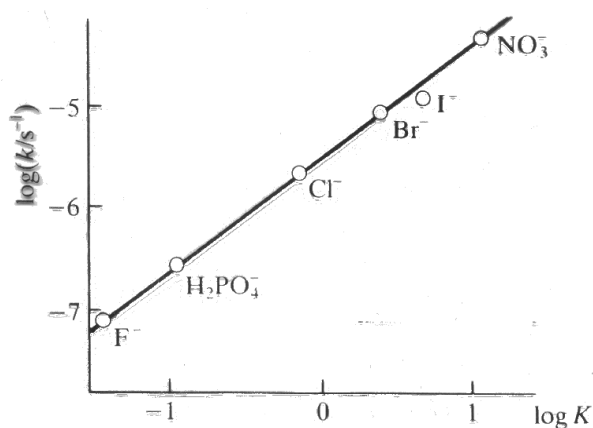
4.2.2. Further evidence for Id mechanisms (Part b) - The effects of spectator ligands

(a) There are no specific cis and trans ligand effects, unlike in the case of substitution at square planar metal centres. Both cis and trans ligands affect substitution rates in proportion to the strength of the M-X bonds they produce.

For the following nickel substitution reaction the reaction is much faster for L = NH$_3$ than for L = H$_2$O.

$$[NiL_5X]+ + H_2O \longrightarrow [NiL_5(H_2O)]^{2+} + X^-$$
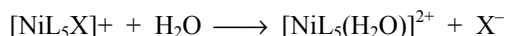
The explanation for this is that NH$_3$ is a stronger σ-base than H$_2$O, and NH$_3$ thus increases electron density at the metal. In the transition state the good donor ligand stabilises the lower coordination number. This observation thus implies a dissociative (I$_d$) reaction.
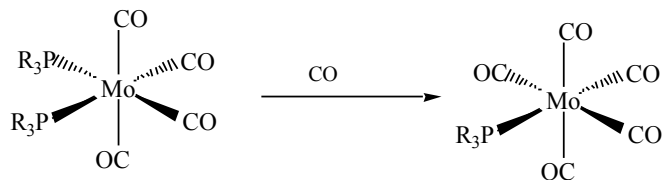
$$PPh_3 > PPh_2Me > PPhMe_2$$

(b) steric effects. Rates are expected to increase with increasing ligand size for D or I$_d$ mechanisms The order of rates of this reaction is PPh$_3$ > PPh$_2$Me > PPhMe$_2$
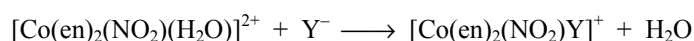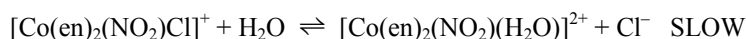
The mechanism is this case may be nearer to D than I$_d$. The mechanism of substitution reactions of organometallic complexes of the transition metals will be discussed in more detail later in this course.

4.2.3. Octahedral substitution - Summary points so far

- Rates of substitution of aquo complexes cover 18 orders of magnitude
- Rate correlates with charge / size ratio for non transition metals - consistent with a dissociative (I$_d$) mechanism
- The pure dissociative (D) mechanism is rare - water is a very good ligand and is usually used as a 55M solution.
- For transition metals there is a switch between I$_a$ and I$_d$ across the series
- For transition metals, CFAE appears to play a significant role in determining rate.
- d^3 and low spin d^8 configurations are inert (Cr^{3+} and Co^{3+} respectively)

## 4.2.4. Base hydrolysis of Co(III) complexes - introduction

In the ligand substitution reactions of octahedral complexes in aqueous solutions there is little or no evidence that one ligand is ever directly substituted by another ligand. The substitution of one X ligand (X not H$_2$O) by a ligand Y (where Y is not H$_2$O) always occurs via the initial replacement of X by H$_2$O. This observation is unsurprising given the concentration of H$_2$O ligands in bulk water (~ 55M). The following mechanism thus applies for the replacement of Co-Cl by Co-Y:

$$[Co(en)_2(NO_2)Cl]^+ + H_2O \rightleftharpoons [Co(en)_2(NO_2)(H_2O)]^{2+} + Cl^- \quad SLOW$$

$$[Co(en)_2(NO_2)(H_2O)]^{2+} + Y^- \longrightarrow [Co(en)_2(NO_2)Y]^+ + H_2O$$

Thus, for the reaction of [Co(en)$_2$(NO$_2$)Cl]$^+$ with a range of Y$^-$ ligands, the rate of release of Cl$^-$ is independent of the identity or concentration of Y$^-$ (Y = N$_3^-$, NO$_2^-$ or SCN$^-$).

## 4.2.5. Base hydrolysis of Co(III) complexes - the conjugate base mechanism

Hydroxide ions (as the Y$^-$ ligand) behave differently from other nucleophiles, and in basic media, Co(III) complexes having NH$_3$, RNH$_2$ or R$_2$NH ligands show reaction kinetics that are sensitive to the nucleophile.

$$L_5MX + OH^- \longrightarrow L_5M(OH) + X^-$$
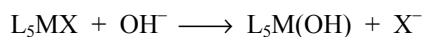
$$rate = k [L_5MX][OH^-]$$

The kinetics of this reaction are clear second order. This observation might suggest (incorrectly) A or I$_a$ mechanisms. Since the hydroxide ion concentration [OH$^-$] is a function of pH, the reaction rate depends on pH. This second order rate law is unique to complexes containing NH$_3$, RNH$_2$ and R$_2$NH ligands. One final feature of this hydroxide substitution reaction is concerned with the ^{16}O/^{18}O isotope distribution in the product.

The origin of ^{16}O/^{18}O isotope effects (^{18}O has 0.2% natural abundance) lies in the following equilibrium:

$$H_2^{16}O + H^{18}O^- \rightleftharpoons H_2^{18}O + H^{16}O^-$$
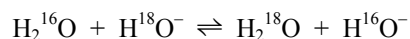
Due to zero point energy effects (go and read your notes on vibrational spectroscopy) the equilibrium constant of this

exchange reaction is not exactly unity (1). This means that water containing OH⁻ ions has a different $^{16}O/^{18}O$ ratio in the H_2O to the $^{16}O/^{18}O$ ratio in the OH⁻ ions. The difference is measurable, and allows us to trace whether the O in a product originates from H_2O or OH⁻. The experimental observation is that the reaction of $[Co(NH_3)_5Cl]^{2+}$ with OH⁻ in water gives $[Co(NH_3)_5(OH)]^{2+}$ which has an isotope distribution characteristic of H_2O and not OH⁻. Thus the OH ligand in the product comes from H_2O and not from OH-.

The mechanism proposed to explain these results involves an initial deprotonation of an NH_3 ligand by an OH⁻ acting as a Brønsted base not a nucleophile, giving the conjugate base of the starting material, hence it is known as the "conjugate base mechanism". C_B or D_{CB}
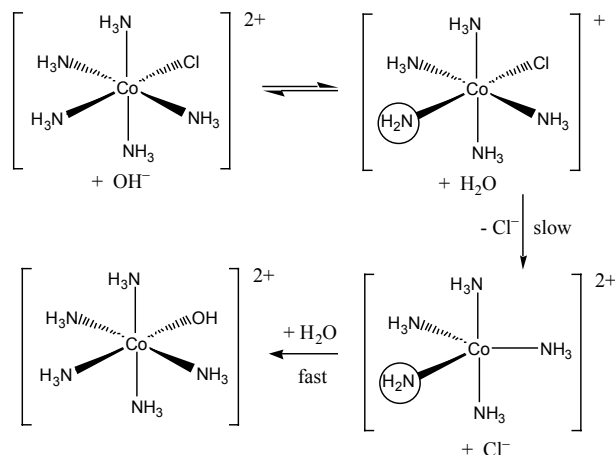
Since the amido group (NR_2) is both a good σ-base and π-base it is able to stabilise the trigonal bipyramid geometry of the transition state, by donation into appropriate metal d orbitals. This greatly accelerates the rate limiting step which is loss of Cl⁻ ion.
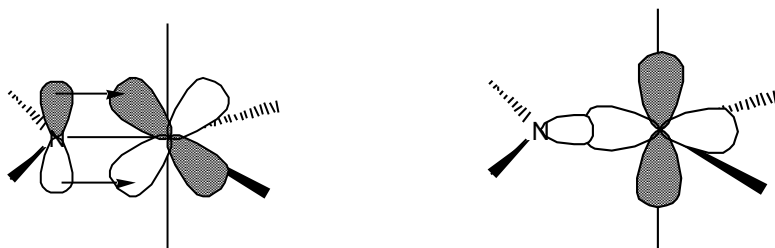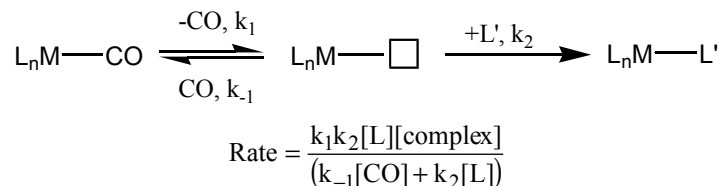

4.3. Ligand substitution in Organometallics

In previous lectures you have met the concepts of ligand substitution in square planar and octahedral complexes containing a wide variety of ligands, but ligands which are not organometallic (metal-carbon bonded). The substitution reactions of square planar complexes proceed via an Associative (A) mechanism. The mechanism of substitution of Octahedral complexes is generally Dissociative Interchange (I_d) although I_a in some cases.

Organometallic chemistry is dominated by the 18 electron rule. In the case of metal carbonyl complexes the 18 electron rule arises since CO is a high field ligand, which bonds to the metal in a synergic fashion (σ-donation and π-backbonding) resulting in a large energy gap between the t_{2g} and e_g levels (in an octahedral complex). The consequence of such a large HOMO-LUMO gap is that 20 electron species are greatly disfavoured.

The reactions of phosphines with metal carbonyls were among the first organometallic substitution reactions studied. The phosphine is usually refluxed with the carbonyl in an organic solvent, such as ethanol or toluene. The dissociative, D, mechanism has been generally observed for 18 electron carbonyls. This involves a slow initial loss of a CO to generate a vacant site at the metal, which is trapped by the incoming ligand L'.

$$L_nM—CO \underset{CO, k_{-1}}{\overset{-CO, k_1}{\rightleftharpoons}} L_nM—\square \xrightarrow{+L', k_2} L_nM—L'$$

$$Rate = \frac{k_1k_2[L][complex]}{(k_{-1}[CO]+k_2[L])}$$

The intermediate is often a highly reactive and therefore a highly unselective reagent. Flash photolysis and ligand competition studies have shown that k_2 is usually of similar magnitude to k_{-1}. The rate equation shown reduces to

$$\text{Rate} = k_1[\text{complex}]$$

if the concentration of CO, and therefore the rate of the back reaction, is negligible. This means that the overall rate is usually controlled by the rate at which the leaving ligand dissociates.

Ligands that bind less well to Cr(0) dissociate faster than does CO. For example, $Cr(CO)_5L$ shows faster rates of substitution of L in the order L = CO < Ph_3As < py. For similar ligands, say phosphines, the larger the cone angle, the faster the dissociation. This mechanism tends to be observed for 18e carbonyls. The alternative, initial attack of a phosphine, would generate a 20e species. While it is not forbidden to have a 20e transition state, the 16e intermediate of Eq. (1) provides a lower energy path in many cases. The entropy of activation of these reactions is positive ($\Delta S = 10 - 15$ eu), as expected for a dissociative process in which the transition state is less ordered. Substitution rates tend to change in the order

$$\text{third row} < \text{second row} > \text{first row,}$$

$$5d < 4d > 3d,$$

and are strongly dependent on metal within a row.

## 4.3.1. How many CO ligands can be replaced?

Phosphines do not replace all the carbonyls in a complex, even in a case where the particular phosphine is sterically small enough to do so. The reaction of $Mo(CO)_6$ with a monodentate alkylphosphine never proceeds further than the fac- $Mo(CO)_3L_3$ stage. This is in part because the phosphines are much more electron donating than the carbonyls they replace. The remaining CO's therefore benefit from increased back donation and are more tightly held in consequence.

fac isomer
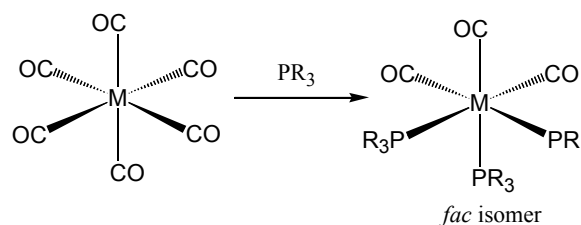
The *fac* stereochemistry , in which the PR_3 ligands occupy a face of the octahedron is preferred to the *mer* arrangement, in which the ligands occupy a meridian. This is because the CO's have a higher trans effect than the phosphines (remember back to the discussion of substitution in square planar complexes, lectures 1 and 2), and so substitution continues until there are no CO's trans to a CO.

Dissociation of ligand is accelerated for bulky ligands. The tetrahedral nickel complex $[Ni(PPh_3)_4]$ is sterically compressed and phosphine dissociation is so facile that the complex is in equilibrium with the tris-phosphine complex.

Dissociation can sometimes be encouraged in various ways. For example, a chloride ligand can often be substituted in the presence of Ag^+, because AgCl is precipitated. However, Tl^+ is used in cases where Ag^+ oxidises the complex and is therefore unsatisfactory. Weakly bound solvents are often useful ligands synthetically, because they can be readily displaced. As a σ-donor, thf is a poor ligand for W(0).

$$W(CO)_5(thf) + PPh_3 \longrightarrow W(CO)_5(PPh_3)$$
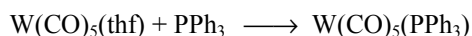
4.3.2. The Associative Mechanism

The slow step in associative substitution is the attack of the incoming ligand L' on the complex to form an intermediate which rapidly expels one of the original ligands L,

$$ML_n \xrightarrow{+L' , k_1} L_nM\text{—}L' \xrightarrow[\text{fast}]{-L , k_2} L_{n-1}M\text{—}L'$$
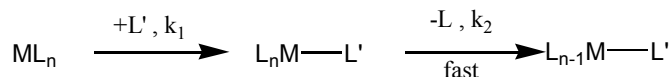
The rate of the overall process is now controlled by the rate at which the incoming ligand can attack the metal in the slow step and so L' appears in the rate equation

$$\text{rate} = k_1[L'][\text{complex}]$$

This mechanism is most frequently adopted by 16e complexes because the intermediate is 18e, and so can usually provide a lower energy route than the 14e intermediate formed in dissociative substitution. The entropy of activation is negative ($\Delta S = - 10$ to $- 15$ eu), as you might expect for the more ordered transition state required. The classic examples of the associative mechanism are shown by 16e, square planar species, such as complexes of Pt(II), Pd(II), and Rh(I). Remember back to lecture 1 and 2, the A mechanism is found for both classical coordination complexes and organometallic complexes of these metals.
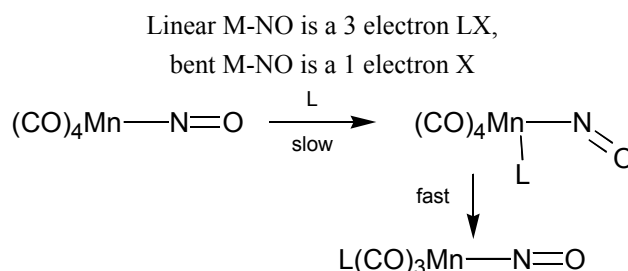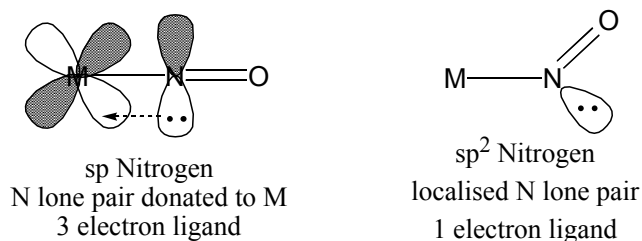
4.3.2.(a). Nitrosyl ligands

Organometallic complexes with 18 electrons can also undergo associative substitution under special circumstances. Such complexes <u>usually contain a ligand capable of rearranging and thus accepting the extra pair of electrons</u>, so that the metal can avoid a 20e configuration. Nitrosyl ligands with their bent to linear rearrangements, are believed to do this.

Recall that a linear nitrosyl is a 3 electron ligand, whilst a bent nitrosyl is a 1 electron ligand.

$Mn(CO)_4(NO)$ shows a second-order rate law and a negative ΔS <u>consistent with an Associative mechanism</u>. This mechanism can be assumed to be operative in ligand substitution reactions of almost all complexes containing nitrosyl ligands.

Second-order rate law and negative $\Delta S^{\ddagger}$

sp Nitrogen
N lone pair donated to M
3 electron ligand

sp^2 Nitrogen
localised N lone pair
1 electron ligand

Linear M-NO is a 3 electron LX,
bent M-NO is a 1 electron X


4.3.2.(b). Cyclopentadienyl ligands

Some (but not all) complexes containing cyclopentadienyl ligands also undergo ligand substitution by an Associative process. A diagnostic test for the Associative process in these complexes is to prepare their analogues where cyclopentadienyl is replaced by indenyl. In such cases, the complex containing an indenyl ligand will undergo associative substitution very much faster than the cyclopentadienyl analogue. This is believed to be a result of the indenyl slipping from an η^5 to an η^3 structure, which is favourable for the indenyl group because the fused benzo ring regains its full aromatic stabilisation energy as the 8- and 9- carbons dissociate from the metal and participate fully in the aromaticity of the benzo ring. These arguments have been strengthened recently by the isolation of several stable complexes with an η^3 or even an η^1 indenyl group, formed by the attack of a ligand on an η^5 indenyl complex. The ligand substitutions of $(\eta\text{-}C_5H_5)Co(CO)_2$ and of $(\eta\text{-}C_5H_5)Re(CO)_3$ (and hence possibly also of $(\eta\text{-}C_5H_5)Mn(CO)_3$) follow this associative mechanism. The indenyl complex reacts much faster with phosphines and the overall rate expression is rate = k_2 [complex][L].

Not all these examples of **Associative** reactions give second-order kinetics; if the ligand rearrangement is rate determining and the incoming ligand (L_i) rapidly traps the open site, we will see first-order kinetics and the substitution will effectively be a dissociative one, because L_i is not involved in the slow step.

Seventeen electron species tend to be much more substitutionally labile than their 18e analogues and usually react by associative pathways via 19e intermediates.

For example, $V(CO)_6$ undergoes second-order ligand exchange at room temperature, while the 18e $[V(CO)_6]^-$ does not lose CO even in molten PPh$_3$.

This means that substitution can sometimes be catalysed by oxidation.

$\eta^5\text{-} \rightleftharpoons \eta^3\text{-} \rightleftharpoons \eta^3\text{-}$
rate = k_2[complex][L].
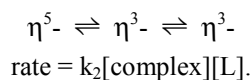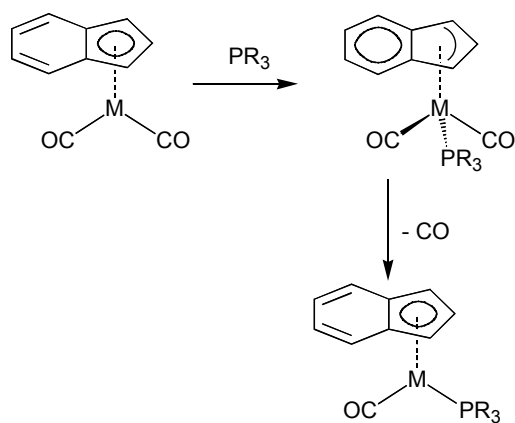
4.3.3. The Interchange Mechanism

There is evidence that certain soft nucleophiles show a second-order, associative component for their substitution even in cases, such as $Mo(CO)_6$, where it is not obvious how the molecule can rearrange to avoid being 20e when the incoming ligand binds.