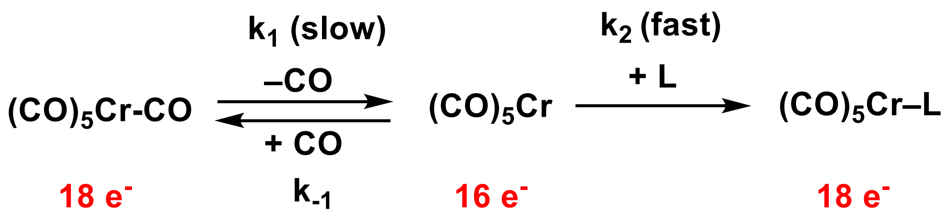
Substitution Reactions

Dissociative (D)

- Generally observed for 18 electron complexes with strong field ligands

- *e.g.* $Cr(CO)_6$, $MnBr(CO)_5$, $Ni(CO)_4$



$\Delta S^{\ddagger}$ = +10 to +15 e.u.

If k_{-1} *is not* important: Rate = $k_1[(CO)_5Cr\text{-}CO]$ = does not depend on [L]

If k_{-1} *is* important: $$\text{Rate} = \frac{k_1k_2[(CO)_5Cr\text{-}CO][L]}{k_{-1}[CO] + k_2[L]}$$

- If $\Delta S^{\ddagger}$ is significantly positive, the mechanism is almost certainly dissociative.

- If the rate does not depend on [L], the mechanism is almost certainly dissociative.

- The *cis*-effect can be used to work out which isomer will be formed in dissociative substitution reactions of octahedral compounds [*e.g.* $MnBr(CO)_5$].

Substitution Reactions

Associative (A)

- Generally observed for 16 and 17 electron complexes
- *e.g.* square planar complexes as well as other geometries

$$\underset{16\ e^-}{L_3IrX + L'} \xrightarrow{k_1\ (slow)} \underset{18\ e^-}{L_3L'IrX} \xrightarrow{k_2\ (fast)} \underset{16\ e^-}{L_2L'IrX + L}$$

$\Delta S^\ddagger = -10$ to -15 e.u.

$\text{Rate} = k_1[L_3IrX][L']$

- If $\Delta S^\ddagger$ is significantly negative, the mechanism is almost certainly associative.

- If the mechanism is associative, the rate of reaction will depend on [L]. However, a dependence of the reaction rate on [L] does not necessarily indicate an associative mechanism.

Square Planar Complexes:

- Associative substitution occurs with retention of configuration.

- The *trans*-effect [made up of the trans influence (a thermodynamic effect) and π-acceptor ability (a kinetic effect)] can be used to work out which isomer will be formed in associative substitution reactions of square planar compounds.

- *e.g.* $[PtCl(NH_3)_3]^+ + Cl^- \rightarrow$ *trans*-$[PtCl_2(NH_3)_2]$; while $[PtCl_3(NH_3)]^- + NH_3 \rightarrow$ *cis*-$[PtCl_2(NH_3)_2]$.

Substitution Reactions

Exceptions: Associative Substitution for 18 electron complexes (negative $\Delta S^{\ddagger}$)

- Certain complexes with π-ligands (*e.g.* cyclopentadienyl, indenyl, fluorenyl):

$$[(\eta^5\text{-Cp})Rh(CO)_2] \xrightarrow[+\ PR_3]{k_1\ (slow)} [(\eta^3\text{-Cp})Rh(CO)_2(PR_3)] \xrightarrow[-CO]{k_2\ (fast)} [(\eta^5\text{-Cp})Rh(CO)(PR_3)]$$

18 e^- | 18 e^- | 18 e^-

- Certain complexes with redox active ligands (*e.g.* NO^+/NO^-, 2 or 4 electron donor alkynes):

$$[(CO)_3Co(NO)] \xrightarrow[+\ PR_3]{k_1\ (slow)} [(CO)_3Co(PR_3)(NO)] \xrightarrow[-CO]{k_2\ (fast)} [(CO)_2Co(PR_3)(NO)]$$

linear NO^+ 18 e^- | bent NO^- 18 e^- | linear NO^+ 18 e^-

Substitution for 17 electron complexes = associative

$$V(CO)_6 + PR_3 \longrightarrow V(CO)_6(PR_3) \longrightarrow V(CO)_5(PR_3) + CO$$

17 e^- | 7 coordinate 19 e^- intermediate | 17 e^-

Rate of substitution: $PMe_3 > P^nBu_3 > P(OMe)_3 > PPh_3$ } **Balance of steric and electronic effects**

- By contrast, 18 electron $[V(CO)_6]^-$ fails to react even with molten PPh_3.

Substitution Reactions

Interchange (I)

- Intermediate between dissociative and associative mechanisms
- $\mathbf{I_d}$ = closer to dissociative mechanism
- $\mathbf{I_a}$ = closer to associative mechanism

$$I_d \quad ML_6 + L' \longrightarrow \underset{\text{intermediate}}{L\text{- - - -}ML_5\text{- - - -}L'} \longrightarrow ML_5L' + L$$

$$I_a \quad ML_6 + L' \longrightarrow \underset{\text{intermediate}}{L\text{-----}ML_5\text{-----}L'} \longrightarrow ML_5L' + L$$

- Dissociative interchange (I_d) → Unlike dissociative mechanism, $\Delta S^{\ddagger}$ is negative and rate always depends on [L].
- Associative interchange (I_a) → Very difficult to distinguish from the associative mechanism.

Cis Effect (for dissociative substitution in octahedral complexes):

$MeCO_2^- > RC(O)^- > SH^- > Cl^- > Br^- > I^- >$ Carbene $> PPh_3 > H^-, CO$

Trans Effect (for associative substitution in square planar complexes – a kinetic phenomenon):

$CO, CN^-, C_2H_4 > PR_3, H^- > Me^- > Ph^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > Py, NH_3, OH^-, H_2O$

Substitution Reactions

Trans Influence (responsible for the ground state contribution to the trans effect):

$H^- > PR_3 > SCN^- > I^- > Me^- > CO > CN^- > Br^- > Cl^- > NH_3 > OH^-$

- Strong σ-donors weaken the metal-ligand bond trans to themselves.

π-Acceptor Ability (responsible for the transition state contribution to the trans effect):

$C_2F_4, NO^+ > C_2H_4, CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$

- Strong π-acceptors greatly prefer an equatorial position in the trigonal bipyramidal transition state formed during associative substitution with square planar complexes (*i.e.* the transition state is lower in energy if the strongest π-acceptor is in an equatorial position → a kinetic effect). See below: