

# Substitution in Octahedral Metal Complexes

(continued)

We have seen that substitution kinetics are influenced by the **metal** in  $I_D$  mechanisms:

- d count effects (Jahn-Teller effects,  $\Delta CFSE$ )
- metal ion charge
- 2<sup>nd</sup> and 3<sup>rd</sup> row effects (slower substitution due to increased M-L bond strength and larger  $\Delta CFSE$ )

*But what about ligand effects?*

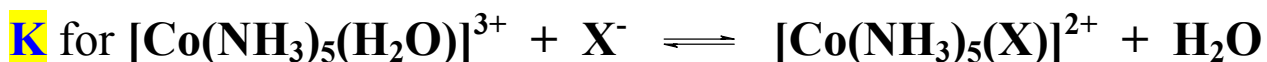
## 1) Entering vs. leaving group effects in an $I_D$ mechanism

- entering group shouldn't matter much (post rate step)



L	log k
F <sup>-</sup>	3.9
SCN <sup>-</sup>	3.8
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	4.3
NH <sub>3</sub>	3.5
H <sub>2</sub> O	4.4

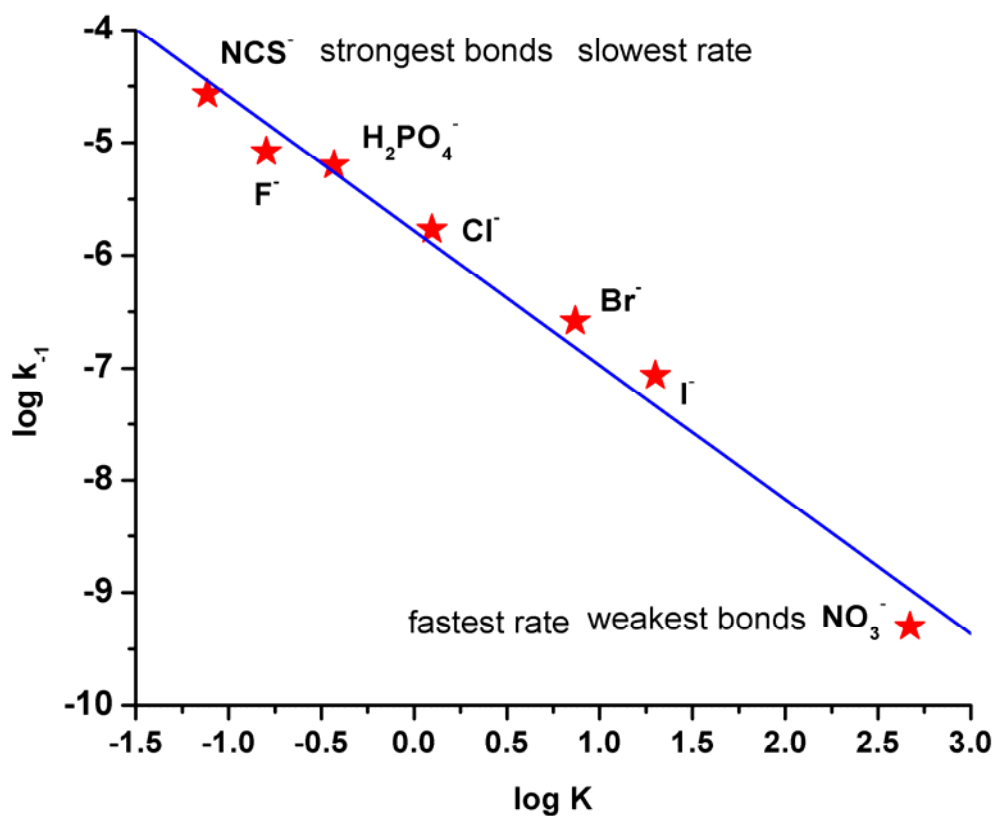
- leaving groups should have a large effect on rate (bond breaking involved in the rate step)



L	k (s <sup>-1</sup> )	K (M <sup>-1</sup> )
NCS <sup>-</sup>	5.0 x 10 <sup>-10</sup>	470
F <sup>-</sup>	8.6 x 10 <sup>-8</sup>	20
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	2.6 x 10 <sup>-7</sup>	7.4
Cl <sup>-</sup>	1.7 x 10 <sup>-6</sup>	1.25
Br <sup>-</sup>	6.3 x 10 <sup>-6</sup>	0.37
I <sup>-</sup>	8.3 x 10 <sup>-6</sup>	0.16
NO <sub>3</sub> <sup>-</sup>	2.7 x 10 <sup>-5</sup>	0.077

- **K** gives a measure of the ground state bond strengths for complexes with X<sup>-</sup> relative to water (**K** = k<sub>1</sub>/k<sub>-1</sub>)
- **k<sub>-1</sub>** gives a measure of the rate of water displacing X<sup>-</sup> (aquation)

Since the M-X bond is breaking in the transition state of aquation in an ID mechanism it **SHOULD** reflect the strength of that bond, as does the equilibrium constant K: a plot of  $\log K$  vs.  $\log k_{-1}$  should therefore be linear (a linear free energy relationship, LFER):

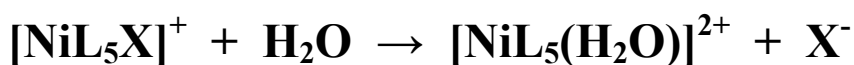


## 2) Effects of spectator (ancillary) ligands on $I_D$ rates

a) transition state is 5-coordinate square pyramidal: metal suffers a loss of electron density relative to the ground state

*How will the electron donating or withdrawing properties of the ancillary ligands affect the rate of substitution of another ligand?*

- better  $\sigma$ - and  $\pi$ -donors will stabilize (lower the energy of) the transition state, increasing the rate of reaction
- $\pi$ -acceptors will destabilize the transition state and slow the reaction down



rate for  $\text{L} = \text{NH}_3 \gg \text{L} = \text{H}_2\text{O}$ ;  $\text{NH}_3$  is a better  $\sigma$ -donor

b) size effects: bigger ligands destabilize higher coordination numbers (i.e. ground state) relative to smaller coordination numbers (i.e. transition state)



## Other indicators of reaction mechanism

*things already mentioned indirectly...*

- **rate laws, order of reaction and sensitivity of rates to identity of the incoming ligand**

### 1) entropy of activation, $\Delta S^\ddagger$

Eyring equation (a theoretical derivation from transition state theory) allows determination of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  by measurement of the T dependence of the rate constant:

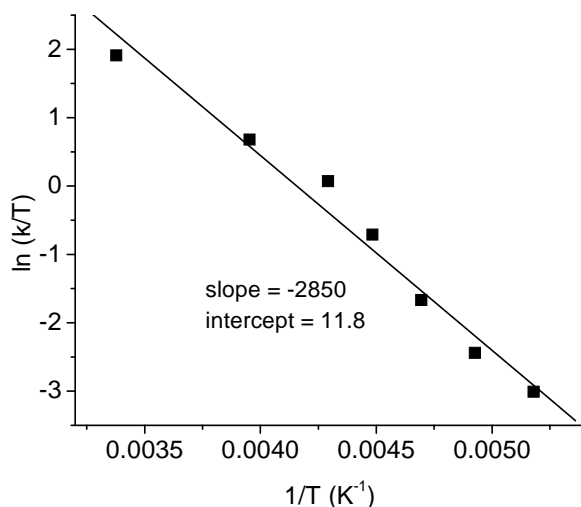
$$\ln(k/T) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R$$

plot  $\ln(k/T)$  vs.  $1/T$  gives a straight line of slope  $-\Delta H^\ddagger/R$  and intercept  $\Delta S^\ddagger/R$  where T is in K and R is the gas constant ( $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$ )

eg.  $\text{Ln}(\text{allox})_3$  (Allox is a bidentate N,O chelate) undergoing isomerization by a Ray-Dutt twist

$$\Delta H^\ddagger = 24 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = +99 \text{ J mol}^{-1} \text{ K}^{-1}$$



- negative entropy of activation implies a more ordered (and presumably associative) transition state
- positive entropy of activation implies a less ordered (and presumably dissociative) transition state

*But careful...*

- errors in  $\Delta S^\ddagger$  are typically very large
- changes in entropy could be due to other effects (differential solvation of the ground and transition state)

## 2) volume of activation, $\Delta V^\ddagger$

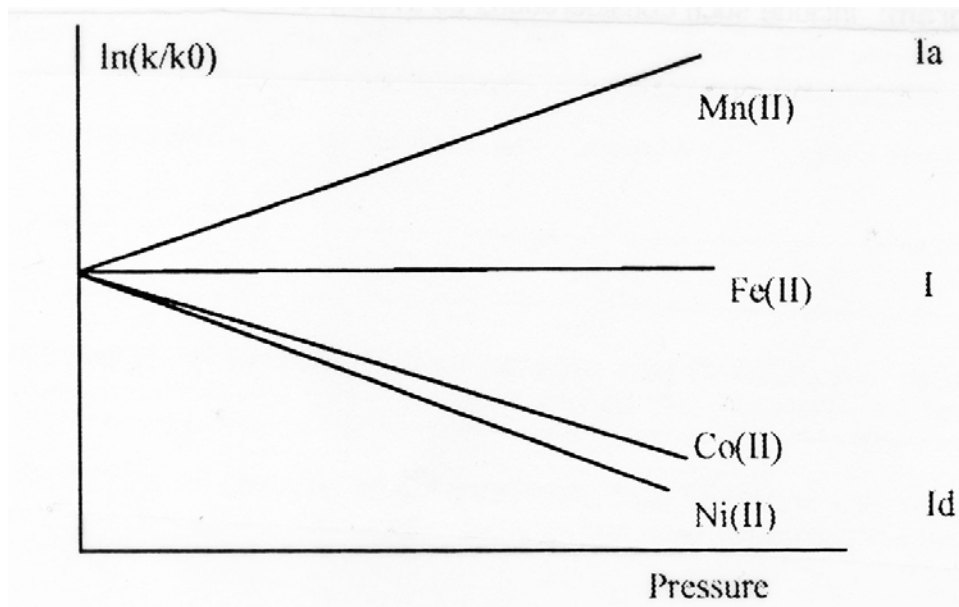
From the pressure dependence of the equilibrium constant:

$$(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT \quad \text{OR} \quad \Delta V^\ddagger = -RT(\partial \ln k / \partial P)_T$$

so the negative of the slope of a  $\ln k$  vs.  $P$  plot gives  $\Delta V^\ddagger$

$\Delta V^\ddagger$  can tell us about volume changes going to the transition state:

- positive volume changes imply  $I_D$  (or D) mechanisms
- negative volume changes imply  $I_A$  (or A) mechanisms



$[\text{M}(\text{H}_2\text{O})_6]^{2+}$	d count	rate	$\Delta V^\ddagger$	mechanism
<b>V</b>	<b><math>d^3</math></b>	<b>87</b>	<b>-4.1</b>	<b><math>I_A</math></b>
<b>Mn</b>	<b><math>d^5 \text{ hs}</math></b>	<b><math>2.1 \times 10^7</math></b>	<b>-5.4</b>	<b><math>I_A</math></b>
<b>Fe</b>	<b><math>d^6 \text{ hs}</math></b>	<b><math>4.4 \times 10^6</math></b>	<b>3.8</b>	<b><math>I_D</math></b>
<b>Co</b>	<b><math>d^7 \text{ hs}</math></b>	<b><math>3.2 \times 10^6</math></b>	<b>6.1</b>	<b><math>I_D</math></b>
<b>Ni</b>	<b><math>d^8</math></b>	<b><math>3.2 \times 10^4</math></b>	<b>7.2</b>	<b><math>I_D</math></b>