Electron transfer reaction

Dilip Debnath



Redox Reaction	Characteristics
1. *Co(NH ₃) ₆ ²⁺ + Co(NH ₃) ₆ ³⁺ ≓ *Co(NH ₃) ₆ ³⁺ + Co(NH ₃) ₆ ²⁺	Extremely slow, $k = (8 \pm 1) \times 10^{-6} M^{-1} s^{-1}$ at 40°C, $\mu = 2.5 M$
2. *Fe(bpy) ₃ ²⁺ + Fe(bpy) ₃ ³⁺ \rightleftharpoons *Fe(bpy) ₃ ³⁺ + Fe(bpy) ₃ ²⁺	$k = 3 \times 10^8 \mathrm{M}^{-1}\mathrm{s}^{-1}$
3. $*Cr^{2+} + CrCl^{2+} \rightleftharpoons$ $*CrCl^{2+} + Cr^{2+}$	$k = 9 \text{ M}^{-1} \text{s}^{-1} \text{ at } 0^{\circ} \text{C}$
4. $Cr^{2+} + Co(NH_3)_5Cl^{2+} + 5 H^+$ $\rightarrow CrCl^{2+} + Co^{2+} + 5 NH_4^+$	$k = 6 \times 10^5 \mathrm{M^{-1} s^{-1}}$, one of earliest examples of an inner-sphere redox reaction
5. $2 \text{ Fe}^{3+} + \text{H}_2 \text{A} \rightarrow$ 2 $\text{Fe}^{2+} + 2 \text{H}^+ + \text{A}$	H_2A = ascorbic acid. Fe(III) complexes formed. Mechanism complicated.
 6. Horse cytochrome-c(II) + Co(phen)³⁺₃ ≓ horse cytochrome-c(III) + Co(phen)²⁺ 	$k = 1.8 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$. Site on protein implicated for binding, different than that used by Fe(CN) ₆ ³⁻ ($k = 9 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$)



Classification of redox reaction

- Outer-sphere process: outer-sphere electron transfer involves intact coordination shell of the reactants.
- Inner-sphere process: In inner-sphere mechanism there are marked changes in the coordination spheres of the reactants.



Characterisation of mechanism: From nature of products

- The eventual products from the reaction are $Cr(H_2O)_6^{3+}[Cr(H_2O)_5Cl]^{2+}, Co(H_2O)_6^{2+}, NH_4^+, Cl^-$
- These could arise from outer sphere mechanism.
 - Then



Taube's classical 1953 experiment (Nobel Prize 1983):

 $\begin{array}{ll} [Co(NH_3)_5Cl]^{2+} + & [Cr(H_2O)_6]^{2+} + 5 H_2O \rightarrow \\ low spin Co(III) & high spin Cr(II) \\ non-labile & labile \end{array}$

 $[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5CI]^{2+} + 5NH_3$ high spin Co(II) Cr(III) labile non-labile Observed rate =6x10⁵ dm³mol⁻¹s⁻¹

Few

- Rate is enormously enhanced
- Chloride ion is transfered to Cr(III) which is very inert, indicating that during the electron transfer Cl⁻ ion has transferred.

Outer-sphere:

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{e^-} Cr^{3+} + Co(NH_3)_5Cl^+$$

$$Co(NH_3)_5Cl^+ \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + Cl^-$$

$$Cr^{3+} + Cl^- \xrightarrow{slow} CrCl^{2+} Rate \approx 10^{-8} dm^3 mol^{-1}s^{-1}$$

•If the electron transfer reaction occurs through outer sphere mechanism then the rate would be much slower than the observed rate ($6x10^5 M^{-1}s^{-1}$).

•Reduction of $[Co(NH_3)_6]^{3+}$ with $[Cr(H_2O)_6]^{2+}$ is slow ($\approx 6x10^{-4}$ dm³mol⁻¹s⁻¹).



Inner sphere mechanism

Rate enhancement and electron transfer accompanied with chloride ion transfer to the reducing agent required to consider that the reaction occurs through a different mechanism

Inner-sphere:

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{\text{bridged}} CrCl^{2+} + Co(NH_3)_5H_2O^{2+}$$

$$Co(NH_3)_5H_2O^{2+} \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + H_2O$$

$$CrCl^{2+} \xrightarrow{\text{slow}} Cr^{3+} + Cl^-$$



 Inertness of [CrCl]²⁺, and lability of Cr²⁺, Co²⁺ are nicely fitted with the proposed inner-sphere mechanism.

Inner sphere mechanism

- – three distinct steps:
- i. substitution to form a bridge between oxidant and reductant. (generally, oxidant possesses bridging ligand that leads to substitution to the reducing center but in some rare cases reductant also provide bridging ligand; eg, reduction of $HCrO_4^-$ with $[Fe(CN)_6]^{4-}$)
- ii. actual electron transfer
- iii. separation of the products (often with transfer of the bridge ligand)





 $[(NH_3)_5Co(H_2O)]^{2+} + [ClCr(H_2O)_5]^{2+}$ high spin Co(II) Cr(III)

3) $[(NH_3)_5Co(\mu-Cl)Cr(H_2O)_5]^{4+} + H_2O \rightarrow$

 $[(NH_3)_5Co(\mu-Cl)Cr(H_2O)_5]^{4+} + H_2O$

1) $[Co(NH_3)Cl]^{2+}$ + $[Cr(H_2O)]^{2+}$ \rightarrow

[(NH₃)₅Co(H₂O)]²⁺ + [ClCr(H₂O)₅]²⁺ high spin Co(II) Cr(III) labile non-labile

followed by a 4th step in this case, because the Co(II) product is substitution labile:

4) $[(NH_3)_5Co(H_2O)]^{2+} + 5 H_2O \rightarrow [Co(H_2O)_6]^{2+} + 5 NH_3$



 $rate = k[I] = \frac{k_1[Ox][Red]}{k_{-1} + k}$

Rate law of ISET process • $Ox-X + Red \underset{K-1}{\overset{k_1}{\longleftarrow}} [Ox-X-Red] \xrightarrow{k} Product$ $k_1[Ox][Red]$

$$Rate = k[I] = \frac{n_1 (on)[100]}{k_{-1} + k}$$

rate limiting steps

- It is possible for any of the three steps to be rate limiting depending on the particular ligand set and metal dⁿ count:
- In Taube's experiment, electron transfer is rate limiting step (because Cr(II) (d⁴, Jahn Teller ion) is substitutionally labile) but...
- replacing Cr(II) with V(II) (d³, inert) as [V(H₂O)₆]²⁺ makes the first step (bridge formation), rate limiting
- Bridge breaking can also be rate limiting step

Evidences

- Rate of reaction: (inertness of CrCl²⁺ and labilities of Cr²⁺ & Co²⁺ are nicely explains the mechanism postulated by H. Taube. Since most of the reactions of Cr²⁺ & Co²⁺ are rapid and most of the reaction of Cr³⁺ are slow.)
- Addition of ³⁶Cl ion in reaction mixture indicated that there is no incorporation of added ion in the product
- Isolation of the bridged complex

Some bridged complexes

Table 5.3 Some Bridged Species Arising from Redox Reactions.¹⁶

Reactants	Species
Cr(II) + Ru(III) chloro complexes	Cr(III) - Cl - Ru(II)
$Co(CN)_{5}^{3-} + IrCl_{6}^{2-}$	Co(III) - Cl - Ir(III)
$Co(edta)^{2-} + Fe(CN)_6^{3-}$	Co(III) - NC - Fe(II)
Cr(II) + V(IV)	$Cr(III) - (OH)_2 - V(III)^a$
$Fe(II) + Co(NH_3)_5 nta$	$Fe(II) - nta - Co(III)^{b}$
Fe(CN) ₅ H ₂ O ³⁻ + Co(NH ₃) ₅ N	(NC) ₅ Fe ^{ll} N



What is the effect of the nature of X

- a) step 1 is rate limiting?
- very little effect since mostly affected by lability of leaving group on partner (assuming ID mechanism is operative)
- b) step 2 is rate limiting?
- some effect because the stronger the bridge, the better electronic effects are transmitted:
- X- order: $F^- < Cl^- < Br^-$, $OH^- < l^-$



Role of ligand

Table 5.7 Rate Constants (k, $M^{-1}s^{-1}$) for the Reduction of Co(NH₃)₅Lⁿ⁺ by a Variety of Reductants at 25 °C

L	Cr ²⁺	V ²⁺	Fe ^{2+ d}	Eu ²⁺
NH ₃	8.0×10^{-5}	3.7×10^{-3}		2×10^{-2}
ру	4.1×10^{-3}	0.24	x	
H ₂ O	≤0.1	0.53		0.15
OCOCH ₃	0.35	1.2	$< 5 \times 10^{-5}$	0.18
ососоон	1.0×10^{2}	12.5	3.8×10^{-3}	
F-	2.5×10^{5}	2.6	6.6×10^{-3}	2.6×10^{4}
Cl^-	6×10^{5}	10	1×10^{-3}	3.9×10^{2}
Br –	1.4×10^{6}	25	7.3×10^{-4}	2.5×10^{2}
I-	3×10^{6}	1.2×10^{2}		1.2×10^{2}
OH-	1.5×10^{6}	<4		$< 2 \times 10^{3}$
N_3^-	$\sim 3 \times 10^{5}$	13	8.8×10^{-3}	1.9×10^{2}
NCS ⁻	19 ^b	0.3	$< 3 \times 10^{-6}$	0.05
<u>s</u> cn-	$1.9 \times 10^{5 \text{ b}}$ $0.8 \times 10^{5 \text{ c}}$	30	0.12	3.1×10^{3}



- i. Containing an unshared pair of electron pair after coordination is minimum requirement for a ligand to be potentially bridging group. (thus $[Co(NH_3)_6]^{3+}$ & $[Co(NH_3)_5Py]^{3+}$ oxidise Cr^{3+} by an outer sphere mechanism.
- ii. Bridging group is very often supplied by the oxidising agent, because this is invariably the inert reagent and bridging group is normally transferred from the oxidant to reluctant (though this is not an essential features ISET [Fe(CN)₆⁴⁻ supplies CN bridge but remains with the iron after electron transfer and breakup]



- iv. Oxidant containing coordinated H₂O ligand a term in the rate law containing an [H⁺]⁻¹ dependency for this reaction is often found
- v. Reduction of $[Co(NH_3)_5X]^{2+}$ by Cr^{2+} , the rate increases with increasing size of the halide ion [exception also arises based on the hard soft concept]
 - iv. Use of oxidant with polyatomic bridging ligand undergoes remote and adjacent attack. (next slide)
 - v. Azide bridging is more effective than isothiosulphate bridging due preference of N bonding over S bonding.
 - vi. There are also double bridging have been established. [Reaction between Cr²⁺ and cis-Cr(N₃)₂⁺ undergoes double bridging



Compared to reduction rate of $[Co(NH_3)_5SCN]^{2+}$ with Cr^{2+} , the reduction of $[Co(NH_3)_5NCS]^{2+}$ by Cr^{2+} is 10^4 times slower. Why? $[Co(NH_3)_5N_3]^{2+}$ is more effective oxidant than $Co(NH_3)_5NCS]^{2+}$ ISET mechanism, why?



Electronic communication through the ligand:

 $\begin{array}{rcl} \left[Fe(CN)_{5}(H_{2}O)\right]^{3-} &+ \left[Co(NH_{3})_{5}(L)\right]^{3+} \rightarrow \\ \hline Fe(II) & Co(III) \\ \\ \left[Fe(CN)_{5}(L)\right]^{2-} &+ \left[Co(NH_{3})_{5}(H_{2}O)\right]^{2+} \rightarrow \\ \hline Fe(III) & Co(II) \end{array}$



k depends on nature of Y: Rate is large if Y = CH=CH, C(O), N, O (conjugated system) small if Y = CH2, CH2CH2 (saturated linkers)

In general, single atoms, small conjugated units like CNor SCN- and larger conjugated π -systems facilitate electron transfer

Mixed inner and outer sphere mechm



Mixed inner and outer sphere mechm

$$\operatorname{Ru}(\operatorname{NH}_3)_5 \operatorname{pz}^{3+} + \operatorname{Co}(\operatorname{edta})^{2-} \xrightarrow{k_1}_{k_{-1}} [(\operatorname{NH}_3)_5 \operatorname{Ru}^{II} \operatorname{pz} \operatorname{Co}^{III}(\operatorname{edta})]^+$$
$$\operatorname{Ru}(\operatorname{NH}_3)_5 \operatorname{pz}^{3+} + \operatorname{Co}(\operatorname{edta})^{2-} \xrightarrow{k_2}_{k_{-2}} \operatorname{Ru}(\operatorname{NH}_3)_5 \operatorname{pz}^{2+} + \operatorname{Co}(\operatorname{edta})^-$$



Redox catalysed substitution

substitutions can be catalysed by the redox process.
(It is most easily detected with inert Cr(III), Co(II) and Pt (IV))
•Hydrolysis, anation and anion interchange all have been accelerated in complexes by the presence of lower oxidation state. For Example:

Chromium(II) catalyzes the ligation of Cr(III)

 $Cr^{II} + X \rightleftharpoons Cr^{II}X$ $Cr^{II}X + Cr^{III} \rightarrow Cr^{III}X + Cr^{II}$

aquation of Cr^{III}X by Cr(II) must catalyse the reverse of the above reaction

- Fe(II) labilises Fe(III)
- Exchange of Co(NH₃)₆ with NH₃/H₂O, catalysed by Co(II) as following path.

 $Co(II) + 6 NH_3 \rightleftharpoons Co(NH_3)_6^{2+}$ $Co(NH_3)_6^{2+} + Co(NH_3)_6^{3+} \rightleftharpoons Co(NH_3)_6^{3+} + Co(NH_3)_6^{2+}$

