CHAPTER 4 Reaction Mechanism of Transition Metal Complexes – II:

Electron Exchange

On the basis of the mechanism involved, the redox reactions of transition metal complexes have been divided into two types: outer-sphere and inner-sphere. We have already studied the same in the previous section. However, these electron-transfer reactions can also be classified on the basis of the metal centers involved as given below.

i) The electron transfer between two different oxidation states of the same metal ion. These reactions are generally called as self-exchange reactions.

ii) The electron transfer between two completely different metal complexes. These reactions are called as the cross-reactions.

The electron exchange or self-exchange reactions may simply be defined as the redox reactions involving the transfer of electrons between two complexes having the same ligands and metal ions but with different oxidation states.

In other words, the reactants in electron-exchange reactions are indistinguishable from the products. These reactions result in no net chemical change and can be studied only by special experimental techniques.

\[
[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + [\text{Fe}^*(\text{H}_2\text{O})_6]^{3+} \rightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + [\text{Fe}^*(\text{H}_2\text{O})_6]^{2+} \tag{14}
\]

\[
[\text{Co}((\text{NH}_3)_6]^{2+} + [\text{Co}^*((\text{NH}_3)_6]^{3+} \rightarrow [\text{Co}((\text{NH}_3)_6]^{3+} + [\text{Co}^*((\text{NH}_3)_6]^{2+} \tag{15}
\]

\[
[\text{Mn}(\text{CN})_6]^{4-} + [\text{Mn}^*(\text{CN})_6]^{3-} \rightarrow [\text{Mn}(\text{CN})_6]^{3-} + [\text{Mn}^*(\text{CN})_6]^{4-} \tag{16}
\]

All of the above are electron-exchange reactions proceeding via the outer-sphere electron transfer mechanism. The rate measurement of these reactions is quite difficult to record as the reactants are chemically equivalent to the products. Out of various techniques such as isotopic tracer, optical activity and EPR-NMR spectroscopy; isotopic labeling is the most convenient and widely accepted method to study the process of self-exchange.

After mixing the reactants, the rate at which the radioactivity disappears in M*(III) complex is the rate of electron exchange in the two complexes. Similarly, the rate at which the radioactivity appears in the M*(II) complexes can also be used to estimate the rate of electron exchange.

![Potential Energy Curves](image)

**Figure 27.** The comparison of potential energy curves of self-exchange and cross-exchange.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Electronic configuration</th>
<th>(k) (M(^{-1})s(^{-1}))</th>
<th>(T) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cr(H_2O)_6)</td>
<td>(t_2g^3e_g^1) (\rightarrow) (t_2g^3e_g^0)</td>
<td>(2 \times 10^{-5})</td>
<td>25</td>
</tr>
<tr>
<td>(Fe(H_2O)_6)</td>
<td>(t_2g^4e_g^2) (\rightarrow) (t_2g^3e_g^2)</td>
<td>4.2</td>
<td>25</td>
</tr>
<tr>
<td>(Co(H_2O)_6)</td>
<td>(t_2g^5e_g^2) (\rightarrow) (t_2g^4e_g^2)</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>(Co(en)_3)</td>
<td>(t_2g^5e_g^2) (\rightarrow) (t_2g^6e_g^0)</td>
<td>(7.7 \times 10^{-5})</td>
<td>25</td>
</tr>
<tr>
<td>(Fe(phen)_3)</td>
<td>(t_2g^6e_g^0) (\rightarrow) (t_2g^5e_g^0)</td>
<td>(1.3 \times 10^7)</td>
<td>3</td>
</tr>
<tr>
<td>(Co(phen)_3)</td>
<td>(t_2g^6e_g^1) (\rightarrow) (t_2g^6e_g^0)</td>
<td>12</td>
<td>25</td>
</tr>
</tbody>
</table>

Now, as the electron-exchange reactions are the simplest type of outer-sphere mechanism; factors like transition-type, orbital overlap, and reorganization of electronic configuration can be used to explain the large differences in the electron-exchange rates listed in Table 2.

In order to get a wider view of the mechanism involved in electron exchange, we need to recall the Frank-Condon principle which says the electronic rearrangements are so rapid that the nuclei can be considered as stationary. Moreover, the electron transfer from one complex to another is expected only when it has the same energy in both of the sites. Hence, the activation energy to achieve this goal is mainly governed by nuclear rearmaments. Consider the following reaction:

\[
[Fe(H_2O)_6]^{2+} + [Fe^{*}(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe^{*}(H_2O)_6]^{2+} \quad (17)
\]

The potential energy curves for the reactants and products should be parabolic because the metal–ligand deformations are almost harmonic in nature. The activated complex is present at the intersection point of the two curves.

![Figure 28](image_url)

\[\text{Fe(II)} \quad \text{Fe}^{*}\text{(III)} \rightarrow \left[ \begin{array}{c} \text{Fe} \\ \text{Fe}\end{array} \right]^{+5} \rightarrow \left[ \begin{array}{c} \text{Fe} \\ \text{Fe}\end{array} \right] \rightarrow \text{Fe(III)} \quad \text{Fe}^{*}\text{(II)}\]

(a)

\textbf{Figure 28. Continued on the next page...}
During the formation of activated complex, the Fe(II) bonds shorten while the Fe(III) bonds lengthen which facilitates the transfer of electron. It is worth noting that the Gibbs free energy change for self-exchange reactions is zero but free energy of activation is still a non-zero term.

Rudolph A. Marcus derived an equation using the first principle to predict the overall rate constant for outer-sphere electron transfer reactions from the self-exchange rate constants of each of the redox couples involved and overall equilibrium constant. The equation can be given as:

$$k = \left( k_1 k_2 K f \right)^{1/2}$$

Where $k_1$ and $k_2$ are rate contents for two electron-exchange reactions and $K$ is the equilibrium constant for the overall reaction. The factor $f$ is a complex parameter composed of the rate constants and has been incorporated to correct the free energy differences of the two reactants. Consider the example,

$$[\text{Fe(CN)}_6]^{4-} + [\text{Fe}^*(\text{CN})_6]^{3-} \rightarrow [\text{Fe(CN)}_6]^{3-} + [\text{Fe}^*(\text{CN})_6]^{4-}$$ (19)

$$k_1 = 7.4 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$$

$$[\text{Mo(CN)}_6]^{4-} + [\text{Mo}^*(\text{CN})_6]^{3-} \rightarrow [\text{Mo(CN)}_6]^{3-} + [\text{Mo}^*(\text{CN})_6]^{4-}$$ (20)

$$k_2 = 3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$$

$$[\text{Fe(CN)}_6]^{4-} + [\text{Mo}^*(\text{CN})_6]^{3-} \rightarrow [\text{Fe(CN)}_6]^{3-} + [\text{Mo}^*(\text{CN})_6]^{4-}$$ (21)

$$K = 1.0 \times 10^2$$
Now, putting the values of $k_1$, $k_2$ and $K$ from equation (19), (20) and (21) in equation (18); the value of rate constant for the overall reaction is found to be $4 \times 10^4 \text{M}^{-1}\text{s}^{-1}$; and it is obviously pretty much comparable to the experimental value of $3 \times 10^4 \text{M}^{-1}\text{s}^{-1}$.

In 1992, R. A. Marcus received the Nobel Prize in the field of Chemistry for his work on the theory of electron transfer reactions occurring in chemical systems. His theory is also named after him, the Marcus theory, and it provides a kinetic and thermodynamic framework for describing outer-sphere electron transfer reactions involving one electron.
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