

Electron Transfer Reactions (Vanessa Frettlöh)

The pioneers on the field of electron transfer are Henry Taube (1915-2005) and Rudolph A. Marcus (Date of Birth: 1923). Both got the Nobel Prize for their work.

According to Taube one can distinguish between **inner sphere** and **outer sphere** reactions. The latter one can be divided into *self-exchange-reactions* (electron transfer between similar corresponding redox centres) and *cross-reactions* (electron transfer between chemically different species). In the outer sphere mechanism the electron transfer takes place when the two redox centres are close enough and the outer sphere complex is built. In the inner sphere mechanism the electron transfer is realized via a bridge-ligand that connects the redox centres.

Marcus Hush Theory (developed since 1956 by R. A. Marcus) is the theoretical basis of the electron transfer reactions. There exist barriers which hinder the electron transfer reactions:

Vibration barrier: the two redox centres have different equilibrium structures and the oxidation number has to change during the reaction. If electron transfer should occur the Franck Condon Principle must be fulfilled (it says that the movement of the nuclei is slow compared to the movement of the electrons. The nuclear positions do not change during the reaction, which is characteristic for a vertical process). Under energy conservation the electron transfer can only take place on the cut surface of the two potential curves. The energy on this surface is equal to the thermal activation energy. The redox centres must have a similar structure if the electron transfer should take place. Therefore the structure of each complex has to change (ligands come closer to or get farer away from the central atom, λ_i inner reorganisation energy). If the distance between the redox centres is high, the vibration barrier will also be high and the electron transfer will be slow.

Solvation barrier: During the complete electron transfer reaction the solvent shell around the complexes will change and this change needs energy which is related to the outer reorganisation energy λ_o . Before the electron can be transferred the solvent shells must change into similar structures.

The basis of the **Marcus parables** is that the free energies of reactants and products are approximately square functions of the reaction coordinate.

$$\Delta G^* = \frac{\lambda}{4} \left[1 + \frac{\Delta G^0}{\lambda} \right]^2 = \frac{[\lambda + \Delta G^0]^2}{4\lambda} \quad \Delta G^0: \text{free enthalpy (is negative)}, \Delta G^*: \text{activation energy}, \lambda = \lambda_i + \lambda_o$$

We can distinguish between three reaction profiles:

- 1.) $(\lambda + \Delta G^0) > 0$: normal Marcus region, reaction rate increases if ΔG^0 increases
- 2.) $(\lambda + \Delta G^0) = 0$: reaction rate reaches a maximum, electron transfer takes place without any activation barrier (diffusion control of the reaction)
- 3.) $(\lambda + \Delta G^0) < 0$: Marcus inverted case, activation barrier increases, reaction rate decreases.

Marcus- Cross- Relation: Rudolph A. Marcus found an equation to describe the electron transfer and to calculate the corresponding rate constant. The fundamental assumption is the additivity of the solvation and vibration barrier of both reactants: $k_{12} = \sqrt{k_{11} \cdot k_{22} \cdot K_{12} \cdot f_{12}}$ (k rate constants, K: equilibrium constant, f: correction term for the difference of the free enthalpies of the two educts).

The most important condition for an **inner sphere mechanism** is a bridge-ligand which can act as Lewis base. In the case of ambident ligands one can distinguish between adjacent and remote attack. There exist two mechanisms for electron transfer via bridge-ligands. One-step-mechanism (redox reaction between the two redox centres only), two-step-mechanism (bridge-ligand is involved in the redox reaction).

Electron transfer reactions can be activated thermally (complex of lower energy is favoured) or photochemically (complex of higher energy is favoured).

Questions:

- 1.) Explain the different types of electron transfer reactions (outer sphere, inner sphere, self-exchange, cross reaction).
- 2.) Draw the three possible reaction profiles and explain where the reaction rate reaches a maximum and why the reactions rates increase or decrease. (Equation is important)