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Marcus equation (for electron transfer)

Relation between the rate of outer-sphere electron transfer and the thermodynamics of this process. Essentially, the rate constant within the encounter complex (or the rate constant of intramolecular transfer) is given by the Eyring equation:

$$k_{\mathrm{ET}} = \frac{\kappa_{\mathrm{ET}}\, k\, T}{h} \exp\left(- \frac{\Delta G^{\ddagger}}{R\, T} \right)$$

where k is the Boltzmann constant, h the Planck constant, R the gas constant and κ_{ET} the so-called electronic transmission factor ($\kappa_{\mathrm{ET}} \sim 1$ for adiabatic and $<< 1$ for diabatic electron transfer). For outer-sphere electron transfer the barrier height can be expressed as:

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta_{\mathrm{ET}} G^{\mathrm{o}})^2}{4\, \lambda}$$

where $\Delta_{\mathrm{ET}} G^{\mathrm{o}}$ is the standard Gibbs energy change accompanying the electron-transfer reaction and λ the total reorganization energy.

Note:

Whereas the classical Marcus equation has been found to be quite adequate in the normal region, it is now generally accepted that in the inverted region a more elaborate formulation, taking into account explicitly the Franck–Condon factor due to quantum mechanical vibration modes, should be employed.

Source:

PAC, 2007, *79*, 293 *(Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006))* on page 368

