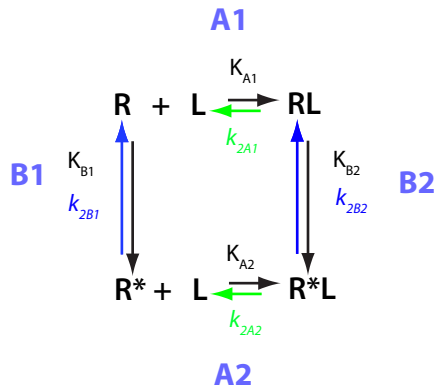


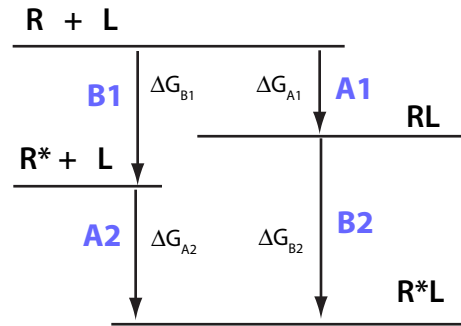
U-R-RL

Binding of one ligand coupled with intramolecular isomerization

Reaction scheme



Free-energy diagram
(positions of energy levels are chosen for easy viewing)



Definitions of relationships between constants and energies (examples)

Equilibrium constant of binding: $K_{A1} = [RL]/[R][L]$

Equilibrium constant of isomerization: $K_{B1} = [R^*]/[R]$

Equilibrium constant expressed in terms of kinetic constants: $K_{A1} = k_{1A1}/k_{2A1}$

Standard free energy difference between the two states:

$$\Delta G_{B1}^{\circ} = G_{R^*}^{\circ} - G_R^{\circ} = -RT \ln(K_{B1}) = -RT \ln([R^*]/[R])$$

Thermodynamic cycle

$$\Delta G_{B1}^{\circ} + \Delta G_{A2}^{\circ} = \Delta G_{A1}^{\circ} + \Delta G_{B2}^{\circ}$$

$$-RT \ln(K_{B1}) - RT \ln(K_{A2}) = -RT \ln(K_{A1}) - RT \ln(K_{B2})$$

$$K_{B1} K_{A2} = K_{A1} K_{B2}$$

We only need to set three equilibrium constants and the fourth will be dependent. To remove this dependent transition from kinetic analysis: set its reverse rate to a very small number, this will set forward rate to a small number too.

My plan

I will assume that I know equilibrium constants for B1, A1 and B2. Dependent constant then is

$$K_{A2} = K_{A1} K_{B2} / K_{B1}$$

If we want to turn that around and assume we know constants for A1, A2, and B1, then for computations

$$I \text{ will use } K_{B2} = K_{B1} K_{A2} / K_{A1}$$