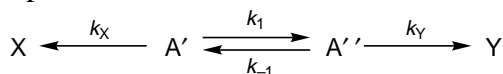


### Curtin–Hammett principle

In a *chemical reaction* that yields one product (X) from one conformational isomer (A') and a different product (Y) from another conformational isomer (A'') (and provided these two isomers are rapidly interconvertible relative to the rate of product formation, whereas the products do not undergo interconversion) the product composition is not in direct proportion to the relative concentrations of the conformational isomers in the *substrate*; it is controlled only by the difference in standard free energies ( $\delta\Delta^\ddagger G$ ) of the respective *transition states*.



$$k_1 \gg k_X \quad k_{-1} \gg k_Y$$

It is also true that the product composition is formally related to the relative concentrations of the conformational isomers A' and A'' (*i.e.* the conformational equilibrium constant) and the respective rate constants of their reactions; these parameters are generally — though not invariably — unknown.

The diagram below represents the energetic situation for transformation of interconverting isomers A and A' into products X and Y.

