

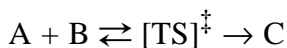
kinetic isotope effect

The effect of isotopic substitution on a rate constant is referred to as a kinetic isotope effect.

For example, in the reaction:



the effect of isotopic substitution in reactant A is expressed as the ratio of rate constants k^l/k^h , where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively. Within the framework of *transition state theory* in which the reaction is rewritten as:



and with neglect of isotopic mass on *tunnelling* and the transmission coefficient, k^l/k^h can be regarded as if it were the equilibrium constant for an isotope exchange reaction between the transition state $[TS]^\ddagger$ and the isotopically substituted reactant A, and calculated from their vibrational frequencies as in the case of a *thermodynamic isotope effect*.

Isotope effects like the above, involving a direct or indirect comparison of the rates of reaction of *isotopologues*, are called ‘intermolecular’, in contrast to *intramolecular isotope effects*, in which a single substrate reacts to produce a non-statistical distribution of *isotopomeric* product molecules.

See also *isotope effect*.

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