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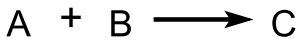
kinetic isotope effect

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 $\frac{k^{\mathrm{l}}}{k^{\mathrm{h}}}$, 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, $\frac{k^{\mathrm{l}}}{k^{\mathrm{h}}}$ can be regarded as if it were the equilibrium constant for an isotope exchange reaction between the transition state $[TS]^{‡}$ 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

Source:

PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1130

