

rate-controlling step

A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite reaction sequence is an elementary reaction the rate constant for which exerts a strong effect — stronger than that of any other rate constant — on the overall rate. It is recommended that the expressions rate-controlling, rate-determining and rate-limiting be regarded as synonymous, but some special meanings sometimes given to the last two expressions are considered under a separate heading. A rate-controlling step can be formally defined on the basis of a control function (or control factor) CF, identified for an elementary reaction having a rate constant k_i by:

$$\text{CF} = \frac{\partial(\ln v)}{\partial \ln k_i}$$

where v is the overall rate of reaction. In performing the partial differentiation all equilibrium constants K_j and all rate constants except k_i are held constant. The elementary reaction having the largest control factor exerts the strongest influence on the rate v , and a step having a CF much larger than any other step may be said to be rate-controlling. A rate-controlling step defined in the way recommended here has the advantage that it is directly related to the interpretation of kinetic isotope effects. As formulated this implies that all rate constants are of the same dimensionality. Consider however the reaction of A and B to give an intermediate C, which then reacts further with D to give products:



Assuming that C reaches a steady state, then the observed rate is given by:

$$v = \frac{k_1 k_2 [\text{A}][\text{B}][\text{D}]}{k_{-1} + k_2 [\text{D}]}$$

Considering $k_2 [\text{D}]$ a pseudo-first order rate constant, then $k_2 [\text{D}] \gg k_{-1}$, and the observed rate $v = k_1 [\text{A}][\text{B}]$ and $k_{\text{obs}} = k_1$. Step (1) is said to be the rate-controlling step. If $k_2 [\text{D}] \ll k_{-1}$, then the observed rate:

$$v = \frac{k_1 k_2}{k_{-1}} [A][B][D] = K k_2 [A][B][D]$$

where K is the equilibrium constant for the pre-equilibrium (1) and is equal to $\frac{k_1}{k_{-1}}$, and $k_{\text{obs}} = K k_2$. Step (2) is said to be the rate-controlling step.

See also: Gibbs energy diagram, microscopic diffusion control, mixing control, rate-determining step

Source:

PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1156

See also:

PAC, 1996, 68, 149 (*A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996)*) on page 182