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least motion, principle of

The statement that those elementary reactions are the most favoured which exhibit the fewest possible alterations in the positions of the atomic nuclei and in the electronic configuration. The most frequently used mathematical formulation of the principle rests on a mechanical model of a molecule in which the energy of structural deformation, when reactants (r) turn into products (p), is assumed to be proportional to the sum of the squares of the changes in the positions of the nuclei common to both reactants and products

$$E = \sum_i f_i (q^{\mathrm{p}_i} - q^{\mathrm{r}_i})^2$$

where f_i is the force constant (in many applications set equal to unity). The equation coincides with the relationship for the potential energy of small vibrations, hence it is valid only at a very early stage of a reaction. This is one of the reasons why many reactions violate the principle of least motion.

Source:
PAC, 1999, *71*, 1919 *(Glossary of terms used in theoretical organic chemistry)* on page 1949

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