A Common Selection Rule for Organic Reactions in Terms of Signs of Direct and Indirect Interorbital Interactions

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The semilocalized approach to chemical reactivity suggested recently is overviewed with respect to both theory and applications. The principal attention is paid to formulation of a common selection rule for organic reactions and to demonstration of its validity to various heterolytic (i. e. nucleophilic and electrophilic) and pericyclic processes. The total energy of the whole reacting system (E) is represented in this approach in the form of power series with respect to all interfragmental interactions (fragments coincide with individual chemical bonds, phenyl rings, etc.). For any reaction, a certain decisive k-th-order energy correction $E_{(k)}$ may be revealed, the sign of which depends on the actual way of the process. The allowed and forbidden reactions are then defined as those described by negative (stabilizing) and positive (destabilizing) corrections $E_{(k)}$, respectively. The condition which ensures the negative sign of $E_{(k)}$ resolves itself into a universal requirement of coinciding signs of the principal direct and indirect interactions of basis orbitals localized on separate fragments (e. g. bond orbitals). This result forms the basis for the above-mentioned selection rule. Allowed (forbidden) ways of heterolytic reactions are exemplified by the back (frontal) attack of a nucleophile upon a substituted alkane in the S_N2 process, the *meta* (*ortho*, *para*) attacks of electrophile upon the pyridine molecule, the addition of electrophile to the C_β (C_α) atom of a donor-containing derivative of ethene (D-C_αH=$C_\beta H_2$), the *trans* (*cis*)-β-elimination processes of substituted alkanes, etc. Application of the same rule to pericyclic reactions is demonstrated to yield predictions coinciding with those of other approaches including the famous Woodward-Hoffmann rule.

Key words: One-Electron Density Matrix; Perturbation Theory; Fragmental Orbitals;
Direct and Indirect Interactions; Semilocalized Approach.