

homodesmotic reaction

A subclass of isodesmic reactions in which reactants and products contain equal numbers of carbon atoms in corresponding states of hybridization; moreover, there is matching of the carbon-hydrogen bonds in terms of the number of hydrogen atoms joined to the individual carbon atoms. To achieve all this matching, one should significantly extend the number and types of reference molecules. In the aliphatic series of hydrocarbons these are propane, isobutane and neopentanes as well as propene and isobutene; for aromatics—buta-1,3-diene, 2-vinylbutadiene (3-methylidenehexa-1,5-diene) and 2,3-divinylbutadiene (3,4-bismethylidenehexa-1,5-diene). Thus to assess strain energy of cyclopropane and aromatic stabilization of benzene the following homodesmotic reactions are to be respectively analysed.



$$\Delta H_{\text{exp}}^0 = -26.5 \text{ kcal/mol (110.9 kJ/mol)}$$



$$\Delta H_{\text{calc}}^0 (\text{MP2/6-31G}^{**}) = 23.9 \text{ kcal/mol (100.0 kJ/mol)}$$

Due to closer matching of the hybridization states of the atoms of reactants and products as compared to isodesmic reactions, the homodesmotic reactions give more accurate estimates of the intrinsic strain and the cyclic delocalization. The definition may be extended to molecules with heteroatoms.

Source:

PAC, 1999, 71, 1919 (*Glossary of terms used in theoretical organic chemistry*) on page 1943