Electronic fluxes during Diels-Alder reactions involving 1,2-benzoquinones: mechanistic insights from the analysis of electron localization function and catastrophe theory.

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Streszczenie

By means of the joint use of electron localization function (ELF) and Thom's catastrophe theory, a theoretical analysis of the energy profile for the hetero-Diels-Alder reaction of 4-methoxy-1,2-benzoquinone 1 and methoxyethylene 2 has been carried out. The 12 different structural stability domains obtained by the bonding evolution theory have been identified as well as the bifurcation catastrophes (fold and cusp) responsible for the changes in the topology of the system. This analysis permits finding a relationship between the ELF topology and the evolution of the bond breaking/forming processes and electron pair rearrangements through the reaction progress in terms of the different ways of pairing up the electrons. The reaction mechanism corresponds to an asynchronous electronic flux; first, the O1-C5 bond is formed by the nucleophilic attack of the C5 carbon of the electron rich ethylene 2 on the most electrophilically activated carbonyl O1 oxygen of 1, and once the σ bond has been completed, the formation process of the second O4□C6 bond takes place. In addition, the values of the local electrophilicity and local nucleophilcity indices in the framework of conceptual density functional theory accounts for the asychronicity of the process as well as for the observed regioselectivity.

Słowa kluczowe

electron localization function, catastrophe theory, Diels-Alder reactions, atom, 2benzoquinines, regioselectivity

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