

First-principle calculations and ab initio direct dynamics study on the molecular mechanism of the 1,3-dipolar cycloaddition reactions

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Abstract: In this work, we reported a systematic investigation by means the theoretical calculations on the regioselectivity and chemical reactivity for a series of the four 1,3-dipolar cycloaddition reactions was studied here using global and local reactivity based on molecular orbital calculations, as well as, also evaluated the thermal effects along the course of the reaction. Here we show that the HOMO energies are, in principle, insufficient to describe the behavior of these chemical reactions at the molecular level, i.e., when there is, for example, the presence of heteroatoms along the pathway of the chemical reaction. By using the frontier effective-for-reaction molecular orbital (FERMO) concept [1-3], the reactions that are driven by HOMO, and those that are not, can be better explained, independent of the calculation method used, because both HF and Kohn-Sham methodologies lead to the same FERMO. On the basis of the localization and the composition of the orbitals can reveal a frontier molecular orbital close to the HOMO energy with a large contribution in atoms present at the active site (APAS), i.e., this special orbital is FERMO. Moreover, the 1,3-dipolar cycloaddition reactions were also studied with the first-principle ADMP molecular dynamics technique at 400 K with the DFT method at level B3LYP with the basis set 6-31 g (d, p) [3]. All calculations were carried out with the Gaussian 09 package [4]. In line with current and previous studies, we find that our approach is adequate to describe qualitative and quantitative concepts on the 1,3-dipolar cycloaddition reactions in light of the FERMO concept and may provide an in-depth understanding of these important reactions.

Acknowledgment

This work has been supported by NanoQC, CAPES, CNPq and Fundação Araucária.

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