

Density functional theory study for the cycloaddition of 1,3-butadienes with dimethyl acetylenedicarboxylate. Polar stepwise vs concerted mechanisms

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The molecular mechanisms for the cycloaddition reactions of four low activated 1,3-butadiene systems (1,3-butadiene, (E)-1,3-pentadiene, (Z)-1,3-pentadiene, and 4-methyl-1,3-pentadiene) with dimethyl acetylenedicarboxylate (DMAD) have been studied using density functional theory methods. For these cycloadditions, two competitive mechanisms have been characterized: the first one corresponds to a concerted C-C bond-formation where the asynchronicity depends on the methyl substitution. The second one corresponds to a stepwise process with a larger polar character where first a C-C bond is formed along the nucleophilic attack of 1,3-butadiene system to a conjugate position of the electron-poor substituted acetylene. Although the nonactivated 1,3-butadiene prefers the concerted process, substitution of hydrogen atoms by electron-releasing methyl groups favors the stepwise mechanism along with an increase of the charge-transfer process. A conformational analysis for DMAD reveals that both pl