

Understanding the reactivity and regioselectivity of [3 + 2] cycloaddition reactions between substituted nitrile oxides and methyl acrylate. A molecular electron density theory study.

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The [3 + 2] cycloaddition (32CA) reactions of three nitrile oxides (NOs) ($R\text{-CNO}$; $R = \text{Ph}$, CO_2Me , and Br) with methyl acrylate (MA) have been theoretically studied within the molecular electron density theory. Topological analysis of the electron localization function of these NOs permits to establish that they will participate in *zw-type* 32CA reactions. Analysis of the conceptual DFT indices indicates that these *zw-type* 32CA reactions will have a low polar character as a consequence of the relatively low electrophilic character of MA and the low nucleophilic character of NOs, in agreement with the global electron density transfer computed at the corresponding TSs. The activation enthalpies associated with these 32CA reactions range from 8.2 to 12.7 kcal·mol⁻¹. The presence of the bromide atom provokes the larger acceleration. While the 32CA reaction involving the CO_2Me substituted NO is highly *ortho* regioselective, the other two reactions are poorly *ortho* regioselective. A bonding evolution theory study of the more favorable *ortho* regiosomeric channel associated with the 32CA reaction involving the Br substituted NO indicates that this reaction is associated to a nonconcerted *two-stage one-step* mechanism, in which the activation energy is mainly related to the initial rupture of the CN triple bond of the NO.

Słowa kluczowe

bonding evolution theory, [3 + 2] cycloaddition reaction, electron localization function, molecular electron density theory

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