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烯酮或乙烯与甲醛环加成协同反应机理的对比研究

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摘要 本文研究了烯酮与甲醛, 乙烯与甲醛两个环加成反应的协同过程的过渡态(TS), 用能量分解方法对两个过渡态中反应物间的相互作用能的本质做了剖析。通过对比, 发现在乙烯与甲的过渡态中反应物的占有轨道间电子的交换排斥作用能比较大, 从而可以说明此反应比乙烯与烯酮间的协同过程难于进行。

关键词 反应机理 乙烯 甲醛 环加成反应 烯酮 协同反应

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A compared study on the concerted reaction mechanism of cycloaddition between formaldehyde and ketene or ethylene

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Abstract The energy decomposition scheme has been used to study the concerted transition state (TS1 and TS2) for the titled reactions. DEF (deformation energy) and the interaction energy components ES (electrostatic energy), PL (polarization energy) and CT (charge transfer energy) for TS1 and TS2 are very similar, but EX (exchange repulsive energy) of TS1 is much smaller than TS2, thus leading to much higher activation barrier for reaction (2), H2C:CH2 + H2CO ?oxirane than reaction (1), H2C:C:O + H2CO ?2-oxooxirane. In order to decrease EX, the reaction (2) has to proceed in two-step (diradical) fashion.

Key words REACTION MECHANISM ETHYLENE FORMALDEHYDE CYCLOADDITION REACTION KETENE CONCERTED REACTION

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