

手性含硫恶唑硼烷催化芳酮不对称还原反应的量子化学研究

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摘要 用HF方法在6-31G^{*}基组下,

对手性含硫恶唑硼烷催化苯乙酮不对称还原反应进行了量子化学从头算研究。还原反应经历了催化剂-硼烷加合物、催化剂-硼烷-酮加合物、催化剂-烷氧基硼烷加合物的生成以及催化剂-烷氧基硼烷加合物的离解过程。催化剂-硼烷加合物、催化剂-硼烷-酮加合物和催化剂-烷氧基硼烷加合物的生成分别为放热、吸热、放热过程;催化剂-烷氧基硼烷加合物离解成催化剂烷氧基硼烷为吸热过程。催化剂-硼烷-酮加合物和催化剂-烷氧基硼烷加合物都存在四种稳定的结构。最有利于氢转移的催化剂-硼烷-酮加合物结构是次低能量结构,并且具有扭曲的船形结构。催化剂-烷氧基硼烷加合物含有一个B-O-B-N四元环,尽管四元环有较大的张力,但加合物仍有较高的稳定性。

关键词 [硫杂环化合物](#) [恶唑硼烷P](#) [催化剂](#) [不对称反应](#) [苯乙酮](#) [还原反应](#) [量子化学](#) [从头算法](#) [手征性](#)

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Quantum chemical study on enantioselective reduction of aromatic ketones catalyzed by chiral sulfur-containing oxazaborolidines

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Abstract In the present paper, the ab initio molecular orbital computations of the enantioselective reduction of acetophenone catalyzed by chiral sulfur-containing oxazaborolidine catalysts are carried out by use of the HF method with 6-31G^{*} basis sets. In the reduction, catalyst- borane adducts, catalyst-borane-ketone adducts, and catalyst-alkoxyborane adducts are generated, and the further decomposition of catalyst-alkoxyborane adducts are generated, and the further decomposition of catalyst-alkoxyborane adducts takes place. The formation of catalyst-borane adducts, catalyst-borane-ketone adducts, and catalyst-alkoxyborane adducts are exothermic, endothermic, and exothermic respectively, whereas the decomposition of catalyst- alkoxyborane adducts into catalyst and alkoxyborane is endothermic. Both catalyst-borane-ketone adducts and catalyst-alkoxyborane adducts have four stable structures. Among the four structures of the catalyst-borane-ketone adducts, the one with the greatest tendency for the hydrogen transfer to take place is the one with the second lowest energy, with a twisted boat structure. Each of catalyst- alkoxyborane adducts contains a B-O-B-N₄-membered ring. In spite of the great tensile stress of the 4-membered ring, the catalyst-alkoxyborane adducts are quite stable.

Key words [SULFUR HETEROCYCLICS COMPOUNDS](#) [CATALYST](#) [ACETOPHENONE](#) [REDUCTION REACTION](#) [QUANTUM CHEMISTRY](#) [AB INITIO CALCULATION](#) [CHIRALITY](#)

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