化学学报 1988 46 (4): 315-320 ISSN: 0567-7351 CN: 31-1320/06

固氮酶底物配位活化的量子化学模拟

刘春万,华建民,卢嘉锡

中国科学院福建物质结构研究所

收稿日期 修回日期 网络版发布日期 接受日期

摘要 用EHMO法就Roussin红盐, MoFeS4(NO)2^2^-, Roussin黑盐及网兜状模型对C2H2,N2, NNH^+和NCH等固氮酶底物的配位活化进行了量子化学模拟.
综合考虑体系总能量与底物多重键的Mulliken键级的变化, 得知乙炔与二核簇相距1.2埃时为最佳活化构型; 在Roussin黑盐及网兜状模型以“架炮"方式与乙炔组成的配位体系中, C≡C键呈5度仰角时为最佳活化构型. 铁比钼更有利于削弱C≡C键. 在N2, NNH^+NCH以“投网"方式与网兜模型组成的配位体系中, 底物的多重键受到较大的削弱. “投网"配位方式使兜口外氮原子上的电荷密度增加, 容易受亲电子试剂的进攻, H^+沿N-N轴线方向攻击N2对活化N≡N键最有利.

关键词 催化剂 乙炔 量子化学 还原 铁络合物 固氮酶 钼络合物 化学键 簇状化合物 分子轨道理论 硫络合物 陆森红盐 陆森盐

分类号 0627 0641

Quantum chemical simulation on the coordination activation of nitrogenase substrates

LIU CHUNWAN,HUA JIANMIN,LU JIAXI

Abstract The coordination activation effects of Red Roussinate, MoFeS4(NO)22-, Black Roussinate, and the string bag model for the nitrogenase substrates (C2H2, N2, NNH+, and NCH) were simulated quantum chem. using EHMO calcns. Considering synthetically the variance of the total energy of the systems and the Muelliken bond orders of the multibonds of substrates, the optimal activation conformations for the system formed from dinuclear clusters and C2H2 is d = 1.2 ? where d is the distance between the CYC bond and MS2M' plane where M is metal atom); for the system formed from Black Roussinate and C2H2 in the cannon mount mode, q = 140? where q is the M-C1-C2 angle. Fe is more favorable than Mo for weakening the CYC bond. In the system formed from the string bag model and N2, NNH+, or NCH in diving mode, the multibond of substrates weakened greatly. In the diving mode the electronic d. of the N atom being out of the mouth of the bag is increased, thus favoring the attack of electrophile. The attack of H+ along the orientation of the N-N axis on the N2 is more advantageous for activating the NYN bond.

Key words CATALYST ACETYLENE QUANTUM CHEMISTRY REDUCTION IRON COMPLEX NITROGENASE MOLYBDENUM COMPLEX CHEMICAL BONDS CLUSTER COMPOUND MOLECULAR ORBITAL THEORY SULFIDE COMPLEX RED ROUSSINATE ROUSSING SALT

DOI:

通讯作者