化学学报 2001 59 (6): 895-900 ISSN: 0567-7351 CN: 31-1320/06

ANTA的结构、性质及其互变异构的理论研究

姬广富,肖鹤鸣,董海山,贡雪东

南京理工大学化学系.南京(210014);中国工程物理研究院化学材料研究所

收稿日期 修回日期 网络版发布日期 接受日期

摘要 对3-硝基-5-氨基-1,2,4-三唑(ANTA)的三种异构体，1H-ANTA(Ⅰ),2－ANTA(Ⅱ)和4H-ANTA(Ⅲ)在，bainitio-HF/3-21G和DFT-B3LYP/3-21G势能面计算的基础上，进行6-311G^**几何参数全优化，MP2总能量和SCRF溶剂(四氢呋喃)效应计算。以振动分析和统计热力学为基础，作标题物热力学性质以及Ⅰ和Ⅱ之间的互变异构反应计算，求得分子几何，电子结构和300～1000K范围的焓、熵和热容以及Ⅰ和Ⅱ互变异构平衡常数和速率常数。发现在三种异构体中在通常温度下以Ⅱ在气相下最稳定，Ⅰ在溶液中最稳定。低温下难以发生异构化反应，温度可提高Ⅰ与Ⅱ之间的互变速率，在800K时两种异构体在气相中等量共存；大于800K时Ⅰ更为稳定。

关键词 动力学 炸药 硝基 氨基 三唑P 从头计算法 互变异构 热力学性质 稳定性 ANTA

分类号 0641

Theoretical study on structures and properties of ANTA and its tautomerization

Ji Anfu,Xiao Heming,Dong Haishan,Gong Xuedong

Nanjing Univ Sci & Technol, Dept Chem.Nanjing(210014)

Abstract The fully optimized molecular geometries and electronic structures of isomers of 5-amino-3-nitrotriazole [1H-ANTA((Ⅰ), 2－ANTA(Ⅱ) and 4H-ANTA(Ⅲ) are obtained by using ab initio method at HF/3-21G level and DFT method at B3LYP/ 6-311G^** level based on the potential energies surface scanning at the HF/3-21G and B3LYP/3-21G level, respectively. The accurate energies at MP2/6-311G^**//HF/ 6- 311G^**level and solavtion effects (in tetrahydrofuran) of three isomers have also been obtained. On the bases of the vibrational analysis and statistical thermodynamic theory, the thermodynamic parameters (enthalpies, entropies and heat capacities) for titled compounds, the equilibrium constants and rate constants of tautomerization of Ⅰ ⟷ Ⅱ from 300K to 1000K, were calculated. The results show that Ⅱ is the most stable among three titled compounds in gaseous state at ordinary temperature, and Ⅰ is the most stable in liquid phase. The tautomerization reaction Ⅰ ⟷ Ⅱ is difficult to occur at lower temperature. The tautomerism rate of 1H- ANTA and 2H-ANTA is up when the temperature increasing. Ⅱ and Ⅰ are equally coexisted in contents at 800K. Ⅰ is more stable than Ⅱ at above 800K.

Key words DYNAMICS EXPLOSIVES NITRO GROUP AMINO GROUP PYRRODIAZOLE P AB INITIO CALCULATION TAUTOMERISM THERMODYNAMIC PROPERTIES STABILITY

DOI:

通讯作者