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论文

S-亚硝基-*N*-乙酰基-*D,L*-青霉胺二肽分子中S—NO键断裂能的测定

李鑫, 程津培

元素有机国家重点实验室, 南开大学化学系, 天津 300071

摘要：

利用滴定量热技术并结合适当的热力学循环测定了乙腈溶液中7个S-亚硝基-*N*-乙酰基-*D,L*-青霉胺二肽化合物中S—NO键的异裂能和均裂能, 其能量范围分别为234.5—246.2 kJ/mol和101.6—122.1 kJ/mol. 结果表明, 所研究的亚硝基硫醇化合物更容易通过S—NO键的均裂释放NO自由基($NO^{\cdot}$). 通过热力学循环对7个亚硝基硫醇化合物自由基负离子中S—NO键的异裂能和均裂能进行估算, 能量范围分别为19.2—35.5 kJ/mol和-4.2—22.6 kJ/mol, 表明这些自由基负离子在室温下不稳定, 容易通过S—NO键的异裂释放出NO^{-}.

关键词： *S*-亚硝基-*N*-乙酰基-*D,L*-青霉胺 S—NO键能 自由基阴离子 滴定量热

Determination of S—NO Bond Dissociation Energies of *S*-Nitroso-*N*-acetyl-*D,L*-penicillamine Dipeptides

LI Xin, CHENG Jin-Pei*

State Key Laboratory of Elemento-Organic Chemistry, Department of Chemistry, Nankai University, Tianjin 300071, China

Abstract:

S-Nitrosodipeptides are generally believed to be good NO donors, and many NO-related biological functions have been directly associated with *S*-nitrosodipeptides, especially in the processes of NO-storage, transport and delivery. In this work, the heterolytic and homolytic S—NO bond dissociation energies of seven *S*-nitrosodipeptides were evaluated *via* titration calorimetry and relative thermodynamic cycles. The energetic scales of the heterolytic and homolytic S—NO bond dissociation energies of these RSNOs covered the ranges 234.5—246.2 and 101.6—122.1 kJ/mol, respectively, which indicated that the studied S-nitrosodipeptides were much easier to release a NO radical($NO^{\cdot}$) rather than a NO cation(NO^{+}). The estimation of the heterolytic and homolytic$(S—NO)^{-\cdot}$ bond dissociation energies of the S-nitrosodipeptides radical anions gave the energetic ranges of 19.2—35.5 and 4.2—22.6 kJ/mol for the$(S—NO)^{-\cdot}$ bond homolysis and heterolysis, respectively, which meant that S-nitrosodipeptides radical anions were unstable at room temperature and favored to releasing a NO anion(NO^{-}) by heterolysis cleavage.

Keywords: *S*-Nitroso-*N*-acetyl-*D,L*-penicillamine S—NO bond energy Radical anions Titration calorimetry

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作者简介:

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