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四唑衍生物异构化反应的理论研究

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摘要 运用MNDOMO法对五种四唑衍生物的互变异构反应进行了理论计算。结果表明,过渡态的几何构型主要由迁移基团所决定,迁移基团的电性对反应速度影响很大。反应活化能与反应物中断裂键的键级和迁移基团上净电荷之间均存在良好的线性关系。二取代基的性质均对反应平衡常数产生影响。

关键词 四唑P 互变异构 活化能 平衡常数 爆炸物

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Theoretical study on tautomerization of tetrazole derivatives

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Abstract Theoretical calculations on the tautomerization of five tetrazole derivatives are performed with MNDO MO method. The results show that the migrating groups (R^2) in the transition states lie above the tetrazole ring planes. The geometries of transition states are determined mainly by R^2 whereas the substituent (R^1) on C(5) hardly affects the geometries. The electron-withdrawing character of R^2 has a great effect on the activation energy while R^1 has fewer effects on it. There are good linear relationships between the activation energies and bond orders of the breaking bonds and the activation energies and charges on R^2 groups in the reactants respectively. The equilibrium constant is affected by the characters of substituents (R^1 and R^2). The greater the electron-withdrawing character of R^1, the larger the equilibrium constant. On the contrary, increasing of the electron-withdrawing character of R^2 makes the equilibrium constant smaller.

Key words TETRAZOLE P TAUTOMERISM ACTIVATION ENERGY EQUILIBRIUM CONSTANT

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