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摘要　本文用能量梯度法,在UHF/3-21G水平上,优化了反应H~2O+CN→HCN+OH的反应物,产物及其过渡态的几何构型,得到了该反应的活化能为32.6kJ/mol, 与实验所得的测量值相一致,同时用Morokuma的数值分析方法,得到了该反应的内禀反应坐标(IRC),沿着IRC,对反应过程中体系构型的变化进行了分析,并计算IRC 运动与垂直于IRC简正振动之间的偶合常数,讨论振动频率的变化,并结合偶合常数进行分子动态学分析,用传统过渡态理论,变分过渡态理论及相关的隧道校正等方法计算该反应的速率常数,结果与实验值基本吻合(如T=763K时,K~(计算值)^(CVT/SCSAG)=3.09×10^1^0,K~(实验值)=(5.1±0.6)×10^1^0,单位为cm^3·mol^-^1·s^-^1)

关键词　水　活化能　反应速度常数　过渡态理论　氰化氢　几何异构　内禀反应坐标法　振动模　选态反应　能量梯度法

Analysis of the IRC and kinetic study for the reaction CN+H~2O→HCN +OH

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Abstract The optimization of the transition state for the reaction CN + H2O ?OH + HCN has been performed by using the energy gradient approach at UHF SCF/3-21G level. The calculated activation barrier of the reaction is 32.6 kJ/mol (exptl. value 31.2 ?0.6 kJ/mol). The Intrinsic Reaction Coordinate (IRC) for the reaction is traced by using Morokuma's magnitude method. Along the IRC, the variations for geometries of the reactants, the coupling constants between the IRC and other normal vibrations, and the changes of the vibrational frequencies are evaluated. By combining the vibrational frequencies with the coupling constants, more dynamic information about the reaction has been provided. The theor. rate constants in the conventional transition state theory, variational transition state theory and tunneling correction approach are calculated and compared with the experimental rate constants over the temperature of 500 ~ 1100 K.

Key words WATER　ACTIVATION ENERGY　REACTION RATE CONSTANT　TRANSITION STATE THEORY　HYDROGEN CYANIDE　GEOMETRICAL ISOMERISM　IRC

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