

Mechanism and Kinetics of the Reaction of Acetylene and Nitric Oxide

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Abstract: The potential energy surface (PES) of a $[C_2H_2N,O]$ system in its electronic doublet ground state has been investigated using density functional theory method, at B3LYP/6-311++G(3df,2p)// B3LYP/6-311++G-(d,p) level. Twelve stable intermediate radicals including trans-nitrosoethenyl 1, cis-nitrosoethenyl 2, iminoketenyl 11, and aminoketenyl 12 radicals have been located. Other stationary points on the PES formed from hydrogen migration and dissociation channels of these intermediates have been identified. Barrier heights, vibrational wavenumbers and moments of inertia were then utilized in the calculations of rate constants using quantum Rice-Ramsperger-Kassel (QRRK) theory. The total rate constant is found to increase with increase of temperature. At temperatures below 1000 K, only a rapid equilibrium is established between the reactants and the trans-nitrosoethenyl 1 radical which, in turn, suggests an absence of a reaction at low temperatures. $HCO + HCN$ is found to be the predominant product at high temperatures and it involves five isomers of $[C_2H_2N,O]$ system as intermediates with the formation of the four-membered ring 3 as the rate determining step. The rate constant for the formation of $HCO + HNC$ is found to be 2 orders of magnitude lower than that for $HCO + HCN$. The total rate constant is pressure independent at low pressures up to atmospheric pressure. The calculated total rate constant at 2000 K and 1 atm pressure is $7.9 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

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