

Electronic structure calculations on the reaction of vinyl radical with nitric oxide

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Abstract: The potential energy surface of the $[C_2H_3NO]$ system in its electronic singlet ground state has been investigated using second-order Møller Plesset perturbation theory (MP2) and coupled-cluster theory CCSD-(T) with the 6-311++G(d,p) basis set. Twenty-six (26) reactive intermediates relevant to the $C_2H_3 + NO$ reaction channel have been identified. Methyl isocyanate 19 is calculated to be the most stable isomer. Two mechanisms (mechanisms A and B) are found to operate competitively toward CH_2O formation, and they include reactive intermediates such as trans-nitrosoethylene 1, cis-nitrosoethylene 2, cyanomethanol 13, isocyanomethanol 14, and the cyclic oxazete 3. While the rate-limiting step in mechanism A is the decomposition of the cyclic oxazete 3, in mechanism B it corresponds to a 1,3-H shift in the trans-nitrosoethylene 1. The potential energies of both these critical transition structures are somewhat higher than the energy of the reactants $C_2H_3 + NO$, which explains the nonobservation of CH_2O in the low-temperature pyrolysis of acetylene in the presence of NO. At low temperatures, the stabilized nitrosoethylenes 1 and 2 will be the dominant products, together with the cyclic compounds 3 and to a lesser extent, also 11. $H_2CO + HCN$ is predicted to be the predominant product at high temperatures. Conversion of NO to CO is kinetically unfavorable due to the high barrier involved in the isomerization of fulminate 15 to isofulminate 16. The most favorable mode of [2+2] cycloaddition between CH_2O and HCN is the one wherein the carbon of the carbonyl group adds on to the nitrogen end of the cyanide.

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