Atmospheric Chemistry Projects

Hydroxyl Reaction with HCF_3

The reactants, products, and the transition state for the reaction $HCF_3 + OH = CF_3 + H_2O$ have been investigated using ab initio molecular orbital theory at the MP2 level. Geometry optimizations and vibrational frequency calculations have been performed on all reactants, products, and the transition state at both the MP2/3-21G** and the MP2/6-311G** levels. Single-point energy calculations at the MP2/6-311G** level using the MP2/3-21G** optimized geometries and at the QCISD/6-311G** level using the MP2/6-311G** optimized geometries have also been carried out on all species. Classical barriers corresponding to these different calculations have been determined and corrected for zero-point energy effects. Transition state theory including tunneling contributions has been used to determine a rate constant which was compared with available experimental data. The QCISD/6-311G**//MP2/6-311G** calculations lead to a classical barrier of 9.589 kcal/mol and a rate constant at 298K (using a non-symmetric Eckart barrier to compute the tunneling correction) of 1.034×10^{-16} cm^3 Molecule^{-1} s^{-1}, in excellent agreement with the best experimental value of 2.1×10^{-16} cm^3 molecule^{-1}s^{-1}. This leads to an estimated lifetime for HCF_3, based on its reaction with OH radicals in the troposphere, of 65.5 yr.

Oxygen Atom Reaction with CF_2O

The reactants, products, and the transition state for the reaction $CF_2O + O = CF_2O_2$ have been investigated using ab initio molecular orbital theory at the MP2 level. Geometry optimizations and vibrational frequency calculations have been performed on all reactants, products, and the transition state at both the MP2/3-21G** and the MP2/6-311G** levels. Most of the calculations have been carried out assuming the oxygen atom was in its lowest triplet state and that the transition state and the product were also in their lowest triplet states. However additional calculations have determined the structure and energy of the singlet ground state of CF_2O_2 and of its lowest singlet excited state. This provides a detailed picture of the thermodynamics of the reaction of CF_2O with either singlet or triplet oxygen to give the singlet, closed shell CF_2O_2.

Chlorine Radical Reaction with Ozone

The reactants, products, and the transition state for the reaction $^1O_3 + {}^2Cl = {}^3O_2 + {}^2ClO$ have been investigated using ab initio molecular orbital theory at the DFT level using the Perdew-Wang functional. Geometry optimizations and vibrational frequency calculations have been performed on all reactants, products, and the transition state

at the pw91pw91/6-31+G* through pw91pw91/aug-cc-pvqz levels. Additional calculations have been carried out using the same levels of theory and basis sets for the reaction $^2ClO + {}^3O = {}^2Cl + {}^3O_2$. These calculations allow us to estimate the rate of these reactions and their importance in ozone depletion processes

Hydroxyl Radical Reaction with Ozone

The reactants, products, and the transition state for the reaction $^1O_3 + {}^2OH = {}^3O_2 + {}^2HOO$ have been investigated using ab initio molecular orbital theory at the DFT level using the Perdew-Wang functional. Geometry optimizations and vibrational frequency calculations have been performed on all reactants, products, and the transition state at the pw91pw91/6-31+G* levels. Additional calculations have been carried out using the same levels of theory and basis sets for the reaction $^2HOO + {}^3O = {}^2HO + {}^3O_2$. These calculations allow us to estimate the rate of these reactions and their importance in ozone depletion processes

Hydroxyl Radical Reaction with Nitrogen Dioxide

The reactants, products, and the transition state for the reaction $NO_2 + OH = NO + HOO$ have been investigated using ab initio molecular orbital theory at the MP2 level. Geometry optimizations and vibrational frequency calculations have been performed on all reactants, products, and the transition state at both the MP2/3-21G** and the MP2/6-311G** levels. Additional calculations have been carried out using the same levels of theory and basis sets for the reaction $HOO + O = HO + O_2$. These calculations allow us to estimate the rate of these reactions and their importance in NO_x depletion and formation processes.