384h Hydrogen Abstraction Reaction of Hydrofluorocarbons by the Hydroxyl Radical. a Hybrid Density Functional Theory with Specific Reaction Parameter Study

Saravanan Swaminathan, Sean Mikel, Donald P. Visco Jr., and Titus V. Albu

Our study focuses on the attack of a hydroxyl radical on the C-H bonds in hydrofluorocarbons (HFCs). This is an important atmospheric process due to increased use of hydrofluorocarbons as substitutes to ozone-damaging chlorofluorocarbons. In recent ab initio and theoretical kinetic studies on these reactions, based on fitting to the experimental rate constants, several groups proposed estimated classical barrier heights for these reactions. We were interested in validating or disputing their proposed values. We carried out calculations of rate constants over a wide range of temperatures using variational transitional state theory. We have performed these calculations using hybrid density functional theory (HDFT) methods to determine the reaction rate constants of hydrogen abstraction from fluoromethanes by hydroxyl radical. The goal is to discover HDFT methods that can be used to calculate the reaction rate constants for these reactions with an 80% confidence with respect to experimental data. We focus on three functionals; (i) BB95, (ii) mPWB95, (iii) mPWPW91, in conjunction with 6 31+G (d,p) basis set, and non-standard Hartree-Fock contributions were optimized for these methods to obtain accurate rate constants. In addition, a number of hybrid density functional theory methods have been used to calculate the classical barrier heights for the hydrogen abstraction reactions of fluoromethanes by the hydroxyl radical. The calculations performed with non-standard Hartree-Fock contributions for the three functionals (mentioned above) provided reaction rate constants within 20% of the experimental values. The use of these new methods is being extended to further investigate more complex HFCs.