Kinetics of the 1-acenaphthyl + O_2 Reaction: A Theoretical Study

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Since about 80% of the energy consumed in the world is produced by various power units using hydrocarbon fuels, polycyclic aromatic hydrocarbons (PAHs) growth and soot formation is one of the major challenges for environmental conservation. One of the key processes of that phenomena is oxidation of soot particles and precursors, which counteracts expansion of those structures. But widely employed reaction models suffer from lack of reliable values for corresponding rate constants and use those for small molecules.

In proposed research, we investigate a reaction between molecular oxygen and 1-acenaphthyl as a model system for oxidation of 5-membered ring embedded in "zigzag"-type edge of soot macromolecule by molecular oxygen. Single-point energies for potential energy surface has been calculated using composite scheme [1] with ab initio calculations at the CCSD(T)/6-311G(d,p) and G3(MP2,CC)//B3LYP/6-311G(d,p) levels of theory. The MESS program package [2] was then used to compute temperature- and pressure-dependent rate constants solving the one-dimensional master equation. Due to different stoichiometry of consecutive steps, we constructed a kinetic scheme of the reaction and a corresponding system of differential equations. This system was solved by the standard means for variety of 1-acenaphthyl and O_2 concentrations and temperatures of interest.

The most preferable path of the reaction leads eventually to formation of 1-naphthyl and consists of two subsequent CO-eliminations. The second one is much faster than the first, which turns out to be rate determining. The ultimate quest of calculation of the total rate constant for reaction 1-acenaphthyl + O_2 → 1 - naphthyl + 2 CO fails because of strong dependency on initial reagents concentrations. Thus, the reaction, in general, should be considered in steps: initial addition 1-acenaphthyl + O_2 → 1 - acenaphthyl peroxy radical and monomolecular dissociation 1 - acenaphthyl peroxy radical → 1 - naphthyl + 2 CO.

1. A .G. Baboul , L.A . Curtiss , P.C. Redfern , K. Raghavachari , Gaussian-3 theory using density functional geometries and zeropoint energies, J. Chem. Phys 110 (1999) 7650–7657
2. Y. Georgievskii, S.J. Klippenstein, Master Equation System Solver (MESS), 2015, available online at http://tcg.cse.anl.gov/papr