Interaction of pyridine radicals with molecular oxygen: Theoretical study

A.S. Savchenkova[1], A. M. Golenko[1], I.V. Chechet[1], S.G. Matveev[1], A.A. Konnov[2], A.M. Mebel[1,3]

[1] Samara National Research University, 34, Moskovskoye shosse, Samara, Russia, 443086
[2] Department of Combustion Physics, Faculty of Physics, Lund University, Lund, Sweden, P.O. Box 118, S-221 00
[3]Department of Chemistry and Biochemistry, Florida International University; Miami, FL, USA, 33199

Around the world, coal-fired power plants continue to play an important role in electricity generation because coal is a less expensive, more abundant and reliable energy resource compared to oil and natural gas. At the same time, environmental issues force strict control over emissions of pollutants from coal combustion. These compounds include, in particular, nitrogen oxides (NOx), which are poisonous to humans. The main nitrogen functional groups in coals are predominantly in the form of heterocyclic aromatic structures, including pyridine and pyrrole rings. In this regard, the pyridine molecule can be considered as a model for studying the transformations of nitrogen during coal combustion. The purpose of this study is to describe the interaction of pyridine radicals with molecular oxygen.

The geometries of reactants, products, intermediatres, and transition states of the reactions of ortho- and meta-pyridyl radicals with O2 were optimized at the level of density functional theory using the ωB97XD functional with the 6-311G** basis set. The vibrational frequencies were calculated at the same level of theory to characterize stationary points as local minima or transition states, to obtain zero-point energy (ZPE) corrections, and for use in partition function calculations. Additionally, the optimized ωB97XD geometries were used to refine single-point energies using the combined ab initio G3(MP2,CC) method.

As a result of the study, it was found that the reactions of ortho-, meta- and para-pyridyls with molecular oxygen have a similar mechanism and give products that are similar in structure. The main pathways of the reactions were studied in detail and potential energy surfaces of the interactions of ortho-, meta- and para-pyridyls with molecular oxygen were constructed.