A Computational Investigation of Oxo-Substituted Peroxy Radicals
Reacting with HO₂ in the Atmosphere

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Introduction

Organic pollutants in the atmosphere are easily radicalized and oxidized to form peroxy radicals. Acetylperoxy is a common organic peroxy radical that often reacts with hydroperoxy radical, a molecule abundant in the troposphere. The three established mechanisms for this reaction are diagrammed below. Each set of products has unique environmental implications.

Singlet Pathway:

Triplet Pathway:

Oxygen Pathway:

Acid Pathway:

Last summer, my lab group focused on locating all of the structures on these reaction coordinates. My goal this past summer was to find a model chemistry that would accurately predict the energies and geometries of these molecules. In order to determine which model chemistry would be the most appropriate for our system, we compared molecules optimized with ten model chemistries to those same molecules optimized with a highly accurate and very computationally costly model chemistry. To ensure that this would accurately reflect their ability to model our system of interest, we chose reactions that are similar to those previously studied using the CASPT2/6-311+G(3df,2p) model chemistry. The reaction pathways are outlined to the right, and the reaction coordinate diagram of the triplet pathway calculated using the CASPT2/6-311+G(3df,2p) is below.

Results and Discussion

We chose to look at the self-reaction of hydroperoxide radical, which had been previously studied using the CASPT2/6-311+G(3df,2p) model chemistry. The reaction pathways are outlined to the right, and the reaction coordinate diagram of the triplet pathway calculated using the CASPT2/6-311+G(3df,2p) is below.

The circled transition structures in the reaction coordinate to the right represent two ways for the intermediate to dissociate into free HOOM and oxygen. Anglada’s study stated that previous computational investigations using model chemistries similar to our’s had only been able to locate one of these structures. During our research, we were able to find both, and their images are shown below.

Finally, below are two graphs of selected data. The graph on the left illustrates how all of our levels of theory combined with the def2TZVP basis set overestimate the bond lengths of intermediate complexes compared to Anglada’s more accurate multireference model chemistry. The graph on the right compares the relative errors of all ten of our model chemistries.

References


Update and Future Work

This Fall- After limiting our focus to the four model chemistries (PBE1PBE and B3LYP, each with both basis sets) that were able to locate both TS3-T and TS3–T, we applied an eleventh model chemistry, B3LYP/6-31+G(d,p). Of these five, B3LYP/6-31+G(d,p) had the lowest average relative error and was carried forward. Run Simulations– Use completed pathways optimized with B3LYP/6-31+G(d,p) and data on all of the conformers in kinetic simulations in order to predict relative reaction yields.

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