

A Computational Study of the 1,3-Cycloaddition of Ozone to Thiophenol: The Structure and Stability of the Primary Ozonides (POZ)

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Ozone plays important roles in daily life processes. Its physical and chemical properties are indispensable in protecting the earth surface from the sun's harmful ultraviolet radiation. And its usefulness as a disinfectant as well as an oxidant in drinking water processing cannot be overemphasized. Many experiments have been done to elucidate the mechanism of ozone reaction in the atmosphere and also in aqueous solution. An important outcome from such experiments is that mechanisms based on kinetic and product studies alone are prone to some errors [1,2]. For example, in the reaction of ozone with phenolic compounds, there is often lack of material balance and in some cases, secondary reactions take place where products react with ozone as well. Consequently, electronic structure calculations can be used to predict reaction mechanisms and complement results derived from experimental studies. Such combination of experimental and theoretical work has been done for the reaction of ozone with phenol [1-3].

In the current computational study, we present the results obtained from the reaction of ozone with thiophenol. Specifically, the structure and the stability of the primary ozonides (POZ) of thiophenol are investigated using density functional theory (DFT) and the coupled-cluster [CCSD(T)] approximation in conjunction with the 6-311+G(d) basis set. This study also investigates the transition states connecting the reactants to the POZs. The calculated Δ_rH and Δ_rG suggest that POZs obtained by adding ozone to the 1,2-, 2,3-, and 3,4-, positions of the thiophenol ring are stable relative to the reactants. However, the binding energies of the thiophenol POZs are lower than the corresponding phenol analogues. Early transition states are computed for the 2,3- and 1,2- POZs while the transition state leading to the 3,4- POZ is late. In all the POZs, the carbon rings are found to be nearly planar.

References

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