Theoretical studies on the reactions of radicals with atmospheric compounds containing reduced sulfur

Abstract

The Earth's radiation balance is the key factor determining climate. The main atmospheric influence on radiative balance are gases such as methane or carbon dioxide, as well as biogenic and anthropogenic aerosols. These aerosols interact directly with incoming radiation and indirectly as Cloud-Condensation Nuclei (CCN). Shaw proposed that oxidized sulfur gases, mainly dimethyl sulfide (DMS), represent the largest component of the biogenic aerosols [Shaw, G., Climatic Change, **1983**, 5, 297]. DMS evaporates from the oceans into the atmosphere, where it is oxidized to form \( \text{SO}_2 \), \( \text{H}_2\text{SO}_4 \), sulphate and Methane Sulphonic Acid (MSA) aerosols. Because of their polar nature, these aerosols function as CCN and thus, sulfur-containing hydrocarbon oxidation products are a primary source of CCN. Therefore, it is necessary, to not only understand the DMS chemical reaction mechanisms with different molecules abounding in the atmosphere, but also to consider the reactions of other sulfur compounds that participate in the generation of aerosols and CCN.

The focus of this work is a study of the primary reactions of various radicals with DMS, dimethyl disulfide (DMDS) and methanethiol (MeSH), which are thought to be the biggest atmospheric source of compounds containing reduced sulphur. For DMS, DMDS and MeSH compounds, the most important oxidation agents are the hydroxyl radical \((\text{OH})\) and the nitrate radical \((\text{NO}_3)\). Additionally, the reactions of DMDS and MeSH with \(\text{CF}_3\) and the \(\text{CH}_3\) radicals will be considered. A similar analysis of DMS was done by Zhang, *et al.*, [Zhang, H.; Zhang, G.-L.; Liu, J.-Y.; Sun, M.; Liu, B.; Li, Z.-S., *J Comput Chem*, **2010**, 31, 2794]. Also, reactions with other radicals which play a crucial role in the sulfur cycle, such as the halogen monoxides and halogen radicals (for example, \(\text{Cl}\)) will be taken into account.

Most of the prior theoretical research utilized the DFT method with only one type of functional, viz. the hybrid functionals B3LYP, BH&HLYP and recently developed MPW1K. Likewise, only a few types of *ab initio* methods, i.e., MP2, CCSD and CCSD(T), were used previously. In this work, however, the Completely Renormalized Coupled-Cluster method of moments CR-CC(2,3) will be used, due to its established ability to eliminate the failures of CCSD(T) in cases involving nearly degenerate states. In addition, aug-cc-pVDZ and aug-cc-pVTZ basis sets with the CR-CC(2,3) method will be applied to these types of calculations for the first time. In fact, augmented cc-pVXZ type basis sets are considered to be the best for CC methods when working with atoms from the first and second row of the periodic table. Finally, a variety of sulfur-containing hydrocarbons and radicals will be used to develop a method capable of accurate and reliable prediction of rate constants for H-abstraction reactions.

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