J. At. Mol. Sci.
doi: 10.4208/jams.091011.102411a

Vol. 3, No. 4, pp. 323-336
November 2012

Theoretical study on the OH with dimethyl sulfide reaction in the presence of water

Wen-Xue Mao[a,*], Zheng-Wen Long[a], Bo Long[a,b], Yi-Bo Wang[c], Chao-Yun Long[a], Shui-Jie Qin[a], and Shi-Xiong Li[a]

[a] *Department of Physics, Guizhou University, Guiyang 550025, China*
[b] *College of Computer and Information Engineering, Guizhou University for Nationalities, Guiyang 550025, China*
[c] *Key Laboratory of Guizhou High Performance Computational Chemistry, Department of Chemistry, Guizhou University, Guiyang 550025, China*

Received 10 September 2011; Accepted (in revised version) 24 October 2011
Published Online 18 May 2012

Abstract. The gas phase reaction between dimethylsulfide (DMSO) and hydroxyl radical (OH) without and with a single water molecule are investigated employing the quantum chemical calculations at the b3lyp/aug-cc-pvtz and mp2/aug-cc-pvtz levels of theory, respectively. We have been given five paths of OH radical with DMSO (A , B, C, D and E). The geometries and computed energies not only indicate that water molecule produces a catalytic effect for path A and path B, but produces a negative effect for path C, path D and path E. We also give the rate constants to support the above result. We can draw the conclusion that water molecule can influence the reaction process, through forming new molecular compounds.

PACS: 31.15.A-, 31.15.E-, 34.50.Lf

Key words: water molecule, catalytic, rate constant, reaction mechanism

1 Introduction

Dimethyl sulfoxide (DMSO) is an important intermediate product of dimethyl sulfide (DMS) in the atmosphere and has been observed in marine atmosphere [1-6]. In addition, the dimethyl sulfoxide (DMSO) is produced in the reactions of dimethyl sulfide (DMS) with other surrounding compounds such as OH, ClO, BrO, and IO [7-9]. Furthermore, dimethyl sulfoxide (DMSO) has been identified as a great importance compound to be released into the atmosphere by ocean phytoplankton [10-15]. It's the largest natural contributor of sulfur in the troposphere and plays the major role in the global sulfur cycle

*Corresponding author. *Email address:* maowenxue86116@126.com (W. X. Mao)

[16-21]. Therefore, dimethyl sulfoxide ($CH_3S(O)CH_3$) can make significant influence on the earth's radiation balance and climate system.

Dimethyl sulfoxide (DMSO) can react with many common oxidants such as O_3, OH, ClO, Cl and NO_3 in the gas phase [22-26]. In the troposphere, the most important daytime oxidant is the hydroxyl radical (OH) [27, 28] and the night principal oxidant is NO_3 radicals [29, 30]. The reactions of DMS and DMSO with OH in the gas-phase is the focus of many researchs and a large amount of data has been given both experimentally [31-38] and theoretically [39-46]. It suggested that the reaction of gas-phase can occur in two distinct pathways: addition-elimination process and hydrogen abstraction process with distinct reaction products. The products of hydrogen abstraction process is CH_3SOCH_2 (DMSO*) + H_2O. The H-abstraction channel for the reaction between DMSO and OH radical have been studied in the absence and presence of a single water molecule by Jørgensen *et al.* indicating that adding a water can stabilize the transition state and lower the reaction barrier [39]. Water is an important component of earth's atmosphere. Many studies have shown that a single water molecule can serve as a catalyst for some gas-phase reactions [47-63]. Water molecule can affect the reaction process through form hydrogen bonded complexes with other molecules such as $O_3\cdots H_2O$ [64], $HNO_3\cdots H_2O$ [65], $SO_3\cdots H_2O$ [66], $CH_3CHO\cdots H_2O$ [67] and $H_2SO_4\cdots H_2O$ [68] in the atmosphere. Beyond that there is study proved that the concentration of the $HO\cdots H_2O$ complex in the tropospheric is estimated to be 5.5×10^{-4} molecule cm^{-3} [55]. It's necessary to take a deep knowledge that water vapor plays in gas phase reactions and the reaction of $HO\cdots H_2O$ with DMSO also should be taken into account.

Path A, path B, path C, path E and path D have been studied in previous literatures [24, 37-39] ,but there aren't reports for the path B, path E and path D with water. In this work we will analyze the formation of hydrogen-bonded complexes between DMSO and OH in presence of one water molecule and give five paths (path A, path B , path C , path E and path D) of the reaction by OH radical with DMSO. In addition, we will report the results of the investigation of reactions A, B, C, D and E and give the rate constants. At last, a kinetic study will be reported, the five paths reactions results without water are compared with those with water, respectively, to illustrate the catalytic effect of a single water . The reaction of DMSO and OH with an single water (reactions A, B, C, D and E) as follows

$$\mathrm{DMSO\cdots H_2O\ (C1A)+OH\rightarrow DMSO^*+2H_2O} \quad (1A)$$
$$\mathrm{DMSO\cdots H_2O\ (C1B)+OH\rightarrow DMSO^*+2H_2O} \quad (1B)$$
$$\mathrm{DMSO\cdots H_2O\ (C1C)+OH\rightarrow DMSO^*+2H_2O} \quad (1C)$$
$$\mathrm{DMSO\cdots H_2O\ (C1A)+OH\rightarrow CH_3SO(OH)+CH_3} \quad (1D)$$
$$\mathrm{DMSO\cdots H_2O\ (C1A)+OH\rightarrow CH_3SO+CH_3OH} \quad (1E)$$