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*

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.

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
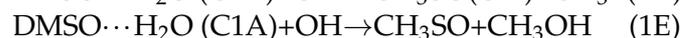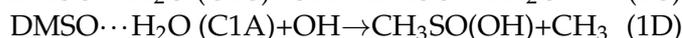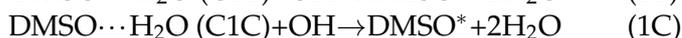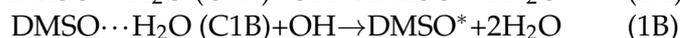

[16-21]. Therefore, dimethyl sulfoxide ($CH_3S(O)CH_3$) can make significant influence on the earth's radiation balance and climate system.

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 day-time 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

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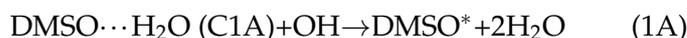
2   Computational details

All the electronic structure calculations are performed using the Gaussian 09 programs [69]. The geometric structure of all the reactants, pre-reactive complexes(M), transition states (TS), product complexes (PC) and products are optimized at the b3lyp/aug-cc-pvtz and wb97xd/aug-cc-pvtz level of theory and the relevant frequencies are calculated at the same level to prove the characters of the transition states with one imaginary frequency and desired reactants , pre-reactive complexes, product complexes and products without imaginary frequency. Jørgensen *et al.* had optimized the similar reaction of DMSO+OH+H_2O using the b3lyp/aug-cc-pvtz level of theory and the results was excellent agreement with the experimental results [39].

In order to obtain the reliable relative energies, single point energies are refined using the mp2/aug-cc-pvtz method at the b3lyp/aug-cc-pvtz-optimized geometries. Because basis sets of the method could be more complex than the MP2/cc-pVTZ that Jørgensen *et al.* has used , the calculated results are provided in Table 1 which indicates that the the mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz theoretical method can exactly produce the binding energy of the DMSO···OH complex than that obtained at the mp2/cc-pvtz//b3lyp/aug-cc-pvtz theoretical approach.

The reaction of DMSO and hydroxyl radical can proceed via five different channels. To obtain the global reaction rate constant for the five paths at 298 K, we applied the conventional transition state theory (CTST)

$$K(T) = k\sigma \frac{k_b}{h} \frac{Q_{TS}}{Q_R} \exp[-(E_{TS}-E_R)/k_bT]$$

where k is the transmission coefficient, Q_{TS} and Q_R are the standard molar partition function per unit of volume for the transition states and the reactants, respectively, taken from the quantum mechanical calculations. k_b is the boltzmann's constant, h is the Planck's constant, and σ is the symmetry factor. E_{TS} and E_R is the energy of the transition state and the reactants, the difference of $E_{TS}-E_R$ is the barrier energies. Taking into account K, the one-dimensional Wigner [44] correction

$$k = 1 + \frac{1}{24} \left(\frac{hv}{k_bT}\right)^2$$

where the v is the imaginary frequency of the transition state.

3   Results and discussion

In the present work we discuss the five reactions of DMSO+OH in the absence and presence of one water molecule. We give the energy profiles and corresponding structures without water for the DMSO and OH reactions in Fig. 1, Fig. 3 and Fig. 5. The energy profiles and corresponding structures with water are demonstrated in Fig. 2 and Fig. 4.
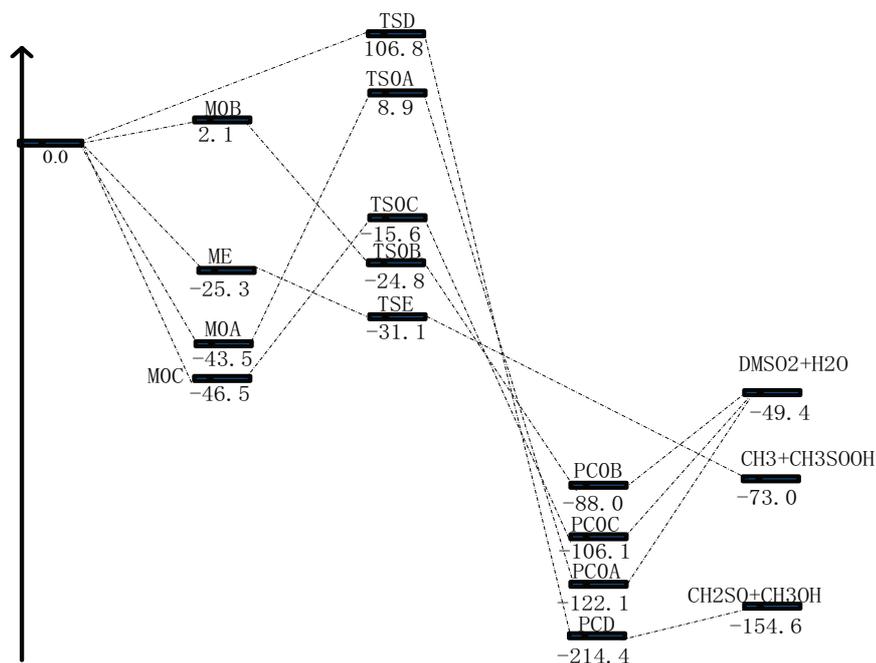
Figure 1: The calculated potential energy profile without water at the mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory (kJ/mol).

We use the symbols M, TS, and PC refer to the reactant complex, transition state and product complex, the number 0 or 1 indicates the number of water molecules present in the reaction. There are three paths that the OH radical can abstract hydrogen atom of the methyl group at out-of-plane (path A and path B) or an in-plane (path C) where the plane is defined by the C-S-C atoms. The three types is refined like these: the hydrogen (a) atoms is abstracted by OH is refined to path A , the following is the same that refined path B and path C. The S···C bond breaking path is path D which is also an S_N2 pathway. Path E is an addition-elimination channel.

The energy of these reactions have been corrected for ZPVE. All the energy values for the five paths are listed in Table 1 and Table 2. The energy barriers and the rate constants for all the reaction are given in Tables 3 and 4.

3.1 Binary system

There are several studies have been reported for the reaction of DMSO+OH without water [11, 39, 46]. In this work we will give five reaction paths of DMSO+OH: path A, path B, path C, path E and path D with water and without water. The reaction without water begins with the formation of the pre-complex (RC0A, RC0B, RC0C, RC0D and RC0E)

and proceed through the transition state (TS0A, TS0B, TS0C, TS0D and TS0E). All the pre-complex and transition state without water are provided in Fig. 3. Compare to the separated reactants, the reactant complexes (ME) is the most stable pre-complex with the energy-49.9 kJ/mol. Because of the a strong bond between the O atom in the OH radical and the S in the S=O group with an O···S length of 1.913 Å , beyond that there are weak interactions between the oxygen atom in the OH radical and H atom in methyl groups with 2.423 Å.

From Table 1 we can easily draw that the energy barriers for the three path A, path D and path E without water, Ea are 8.9 kJ/mol, 106 kJ/mol and -31.1 kJ/mol calculated at mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory ,respectively, in good agreement with previous theoretical results (8.3 kJ/mol,116 kJ/mol and -28 kJ/mol) by González-García *et al.*[11]. Path D in absence of water have the biggest energy barry 106.7 kJ/mol agreeing with previous theoretical results (111.6 kJ/mol) [11]. The energy for products is -49.3 kJ/mol, -173.8 kJ/mol and -57.4 kJ/mol for path A, path E and path D respectively, also in good agreement with the results (-57 kJ/mol 161.8 kJ/mol and -62.8 kJ/mol) by González-García *et al.*[11]. From above, we can see that the chosen calculation method in this work is feasible.
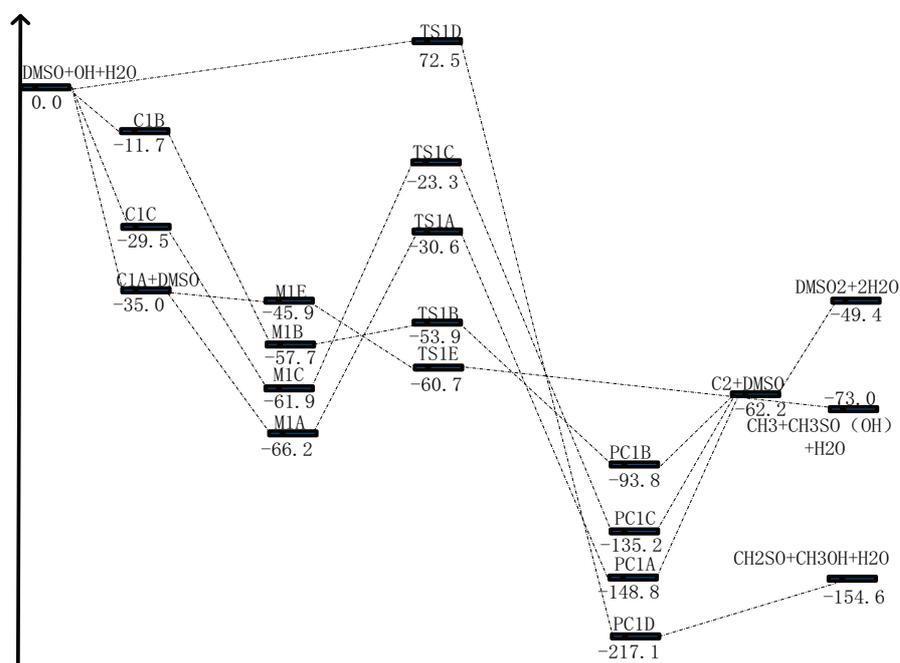

Figure 2: The calculated potential energy profile with water at the mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory (kJ/mol).
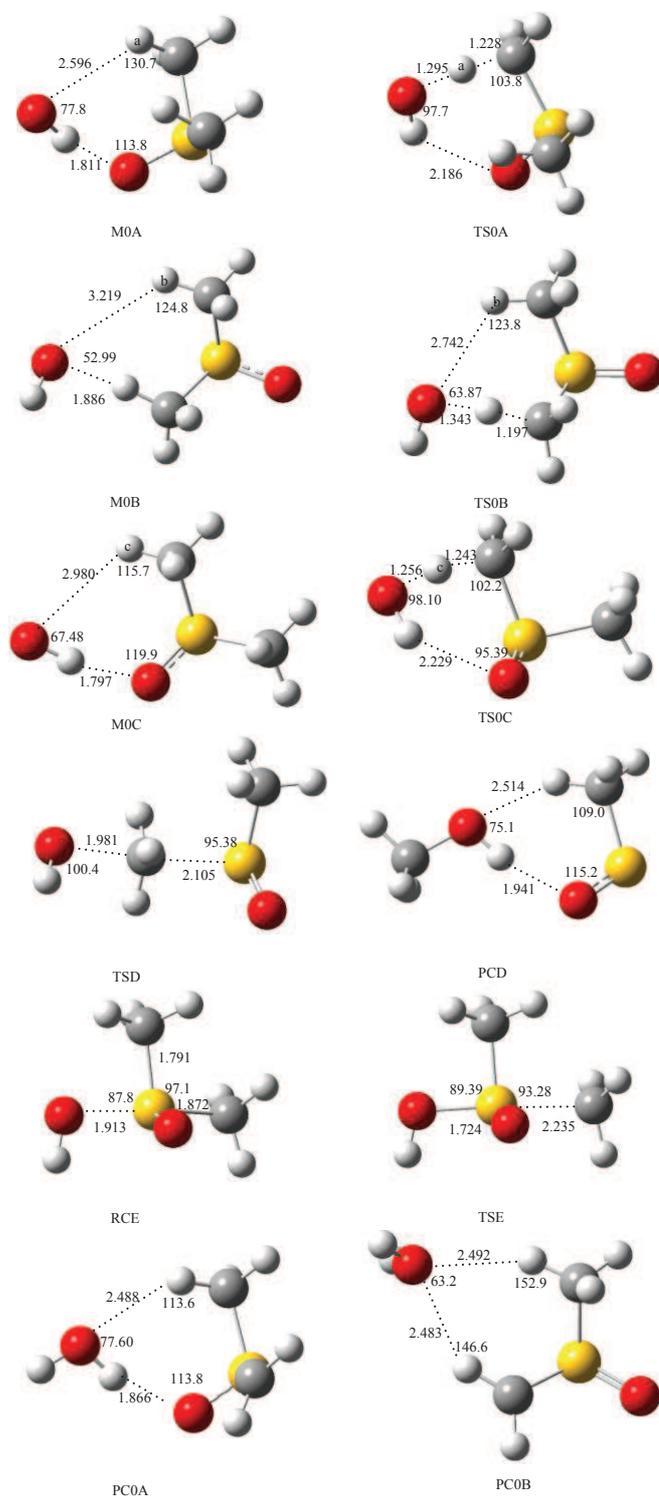
Figure 3: The optimized complexes and transition states without water at the b3lyp/aug-cc-pvtz level level of theory.

Table 1: The reaction and activated energy, enthalpies and free energies for the reactions of DMSO +OH with zero-point correction included at 298 K (kJ/mol).

Species	ΔH^a	ΔG^a	ΔE^a	ΔE^b	ΔE^c
DMSO+OH	0	0	0	0	0
M0A	-34.4	0.4	-31.9	-29.1	-43.5
TS0A	-17.4	23.0	-12.8	-16.8	8.9
PC0A	-94.2	-65.4	-94.5	-92.1	-122.1
M0B	–	–	–	-4.8	2.1
TS0B	-1.9	31.5	0.7	-8.5	-24.8
PC0B	-73.9	-53.6	-77.0	–	-88.0
M0C	–	–	–	-26.5	-46.5
TS0C	-3.2	35.2	0.8	-2.2	-15.6
PC0C	-92.9	-66.3	-93.5	-91.5	-106.1
H2O+DMSO*	-65.6	-72.2	-67.8	-70.4	-49.4
TSD	62.5	96.3	64.5	40.4	106.8
PCD	-194.4	-168.6	-193.9	-198.1	-186.7
CH3SO+CH3OH	-174.5	-187.4	-173.9	-181.7	-154.6
ME	-34.1	4.4	-31.2	-49.9	-25.3
TSE	-27.5	11.1	-24.1	-27.3	-31.1
CH3+CH3SO(OH)	-56.5	-61.4	-57.4	-63.8	-73.0

[a] Calculated at the wb97xd/aug-cc-pvtz level of theory.
[b] Calculated at the b3lyp/aug-cc-pvtz level of theory.
[c] Calculated at the mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory.

3.2 Ternary system

The Reaction mechanism for DMSO has two possible initial reaction forms: $H_2O\cdots DMSO$ and $H_2O\cdots OH$. We have given three different hydrogen-bonded complexes formed with DMSO and water (C1A, C1B, C1C), moreover, we give the calculated values for their geometrical structure and relative energy with water are displayed in Fig. 2, Fig. 4 and Table 2. C1A is the main form in the sea surface [39]. So the path D and path E consider the reaction of C1A + OH. Two of these paths have been recently reported in the literatures and our results for path A are agree well with the reports values [39].

The OH radical can attract on different H atom of the DMSO and make the bond of $C\cdots S$ breaking in the presence of water molecular and absent water molecular. We will analyze the influence of single water molecule on the reaction of DMSO+OH in this part. Water can combine with DMSO and water giving rise to the formation of two possible initial complexes $DMSO\cdots H_2O$ and $HO\cdots H_2O$ which can react with OH and DMSO respectively to influence atmosphere. The reactant complexes ($DMSO\cdots OH\cdots H_2O$) of H-abstraction channel are eight-membered ring structure with three hydrogen bonds. The corresponding transition states TS1A, TS1B, TS1C responsible for the formation of DMSO and water molecular are depicted in Fig. 4. The reactants may be DMSO and

Table 2: The reaction and activated energy, enthalpies and free energies for the reactions of DMSO +OH + H2O with zero-point correction included at 298 K (kJ/mol).

Species	ΔH^a	ΔG^a	ΔE^a	ΔE^b	ΔE^c
$DMSO+H_2O$	0.0	0.0	0.0	0.0	0.0
H_2O+OH	0.0	0.0	0.0	0.0	0.0
$C1(H_2O\cdots OH)$	-18.5	8.2	-15.4	-14.4	-16.0
$C2(H_2O\cdots H_2O)$	-14.1	11.3	-12.1	-10.3	-62.2
$C1A(DMSO\cdots H_2O)$	34.7	-0.1	33.0	-25.4	-35.0
$C1B(DMSO\cdots H_2O)$	-11.7	-10.7	15.6	-5.5	-11.7
$C1C(DMSO\cdots H_2O)$	-27.8	5.9	-26.4	-21.8	-29.5
M1A	-70.5	1.6	-65.5	-55.4	-66.2
TS1A	-58.2	19.4	-51.0	-47.8	-30.6
PC1A	-127.1	-62.4	-125.3	-116.9	-148.8
M1B	-79.8	-4.5	-74.8	-18.3	-57.7
TS1B	-17.4	53.2	-12.5	-23.2	-53.9
PC1B	0.0	0.0	0.0	-76.9	-93.8
M1C	-64.2	4.7	-59.8	-52.6	-61.9
TS1C	-44.8	33.0	-37.7	-36.0	-23.3
PC1C	-124.0	-60.5	-121.9	-116.3	-135.2
$2H_2O+DMSO^*$	-65.6	-72.2	-67.8	-70.4	-49.4
TS1D	33.3	102.6	36.6	20.5	72.5
PC1D	-225.0	-161.9	-222.3	-220.8	-217.1
$CH_3SO+CH_3OH+H_2O$	-174.5	-187.4	-173.9	-181.7	-154.6
M1E	-63.1	10.0	-59.0	61.3	-45.9
TS1E	-54.4	22.0	-48.8	-46.7	-60.7
$CH_3+CH_3SO(OH)+H_2O$	-56.5	-61.4	-57.4	-63.8	-73.0

[a] Calculated at the wb97xd/aug-cc-pvtz level of theory.
[b] Calculated at the b3lyp/aug-cc-pvtz level of theory.
[c] Calculated at the mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory.

the $H_2O\cdots HO$ complex, or the $DMSO\cdots H_2O$ complex with the OH radical. Reaction process is described in the potential energy profile presented in Fig. 4. From Table 1 and Table 2, we can draw that energy barriers calculated at b3lyp/aug-cc-pvtz level of theory are almost smaller than calculated at mp2/aug-cc-pvtz . The energy barriers for the five paths with water is calculated with $E_{TS}-E_{C1}$. E_{C1} refers to $DMSO\cdots H_2O$ (C1A,C1B and C1C). energy barrier of path D with water and without water is the biggest one with the energy 106.8kJ/mol and 107.5 kJ/mol.

3.3 Analysis

The energy profiles and corresponding structures for the five paths with water and without water are showing in Figs. 1-5.

Table 3: Rate constants K (cm^{3}molecule^{-1}s^{-1}), imaginary frequencies(ν) of each transition state(cm^{-1}), the one-dimensional tunneling correction (k) with Wigner and energy barriers (E) for five paths without water at mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory.

Reaction	ν	k	K	E
DMSO+OH				
TS0A	1103	2.1854	$4.9\times10\text{-}16$	8.9
TS0B	640	1.399	$8.54\times10\text{-}10$	-24.8
TS0C	1394	2.896	$1.48\times10\text{-}11$	-15.6
TS0D	759	1.5608	$9.49\times10\text{-}33$	106.8
TS0E	266	1.0692	$1.99\times10\text{-}9$	-30.9

Table 4: Rate constants K (cm^{3}molecule^{-1}s^{-1}), imaginary frequencies(ν) of each transition state(cm^{-1}), the one-dimensional tunneling correction (k) with Wigner and energy barriers (E) for five paths with water at mp2/aug-cc-pvtz//b3lyp/aug-cc-pvtz level of theory.

Reaction	ν	k	K	E
C1A+OH				
TS1A	1121	2.2233	1.02×10^{-15}	4.4
TS1D	782	1.5956	7.18×10^{-33}	107.5
TS1E	271	1.0718	8.61×10^{-10}	-25.7
DMSO+C1				
TS1B	466	1.2118	1.4×10^{-8}	-42.3
TS1C	1425	2.9766	2.453×10^{-16}	6.2

From Fig. 3 and Fig. 4, we can draw that each reaction complex (M) has a cyclic hydrogen bond structure with a strong hydrogen bond interaction between DMSO, OH and H_2O. The water molecule is not only a proton donor that strongly donating a proton to the O atom but also an acceptor that strongly accepting a proton from the DMSO. So proton transfer occurs.

We can obtain that energy barrier is different among path A, path B , path C , path D and path E in the absence and presence of a single water molecule . Path A and path B are similar which are different from path C. The energy barrier of path A with water is found to be 1.05 kJ/mol lower than 8.9 kJ/mol without water, similarly, the energy barrier of path B with water is -10.1 kJ/mol lower than -5.93 kJ/mol without water. On the contrary, it is 1.4 kJ/mol with water bigger than -3.73 kJ/mol without water for the path C. Path A and path B indicate that the single water has influence on reducing the reaction barrier in agree with previous studies [39], path C is unlikely to happen. It's same to path D and path E, the energy barrier of the two paths with water are 25.7 kJ/mol and -6.5kJ/mol, however, it's 25.5 kJ/mol and -7.4kJ/mol for the two paths without water. From above, we can draw that the single water has negative influence on the path D and path E, for the energy barriers increased when the water molecule added.

So we can obtain that the water is only catalyst for path A and path B. The atmospheric
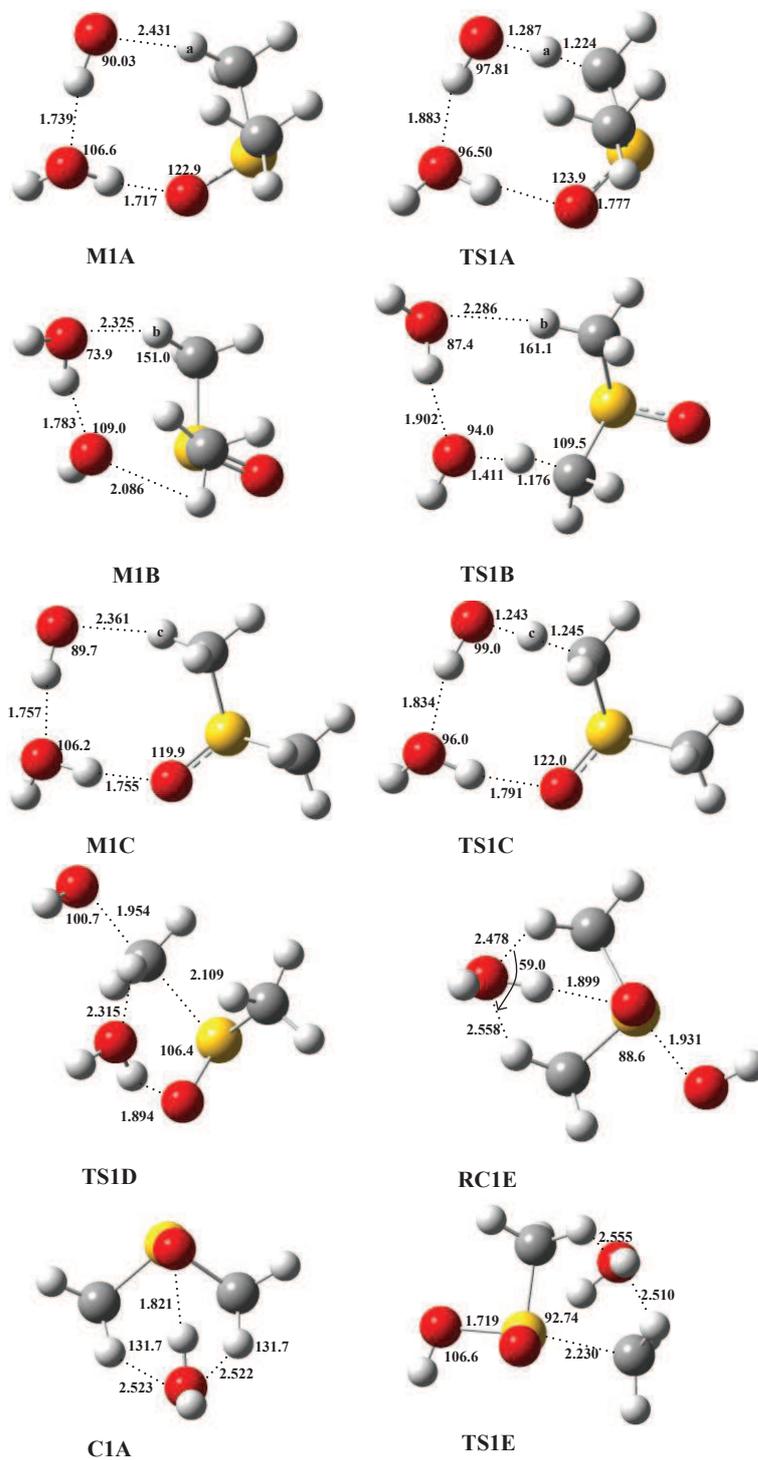
Figure 4: The optimized complexes and transition states with water at the b3lyp/aug-cc-pvtz level level of theory.
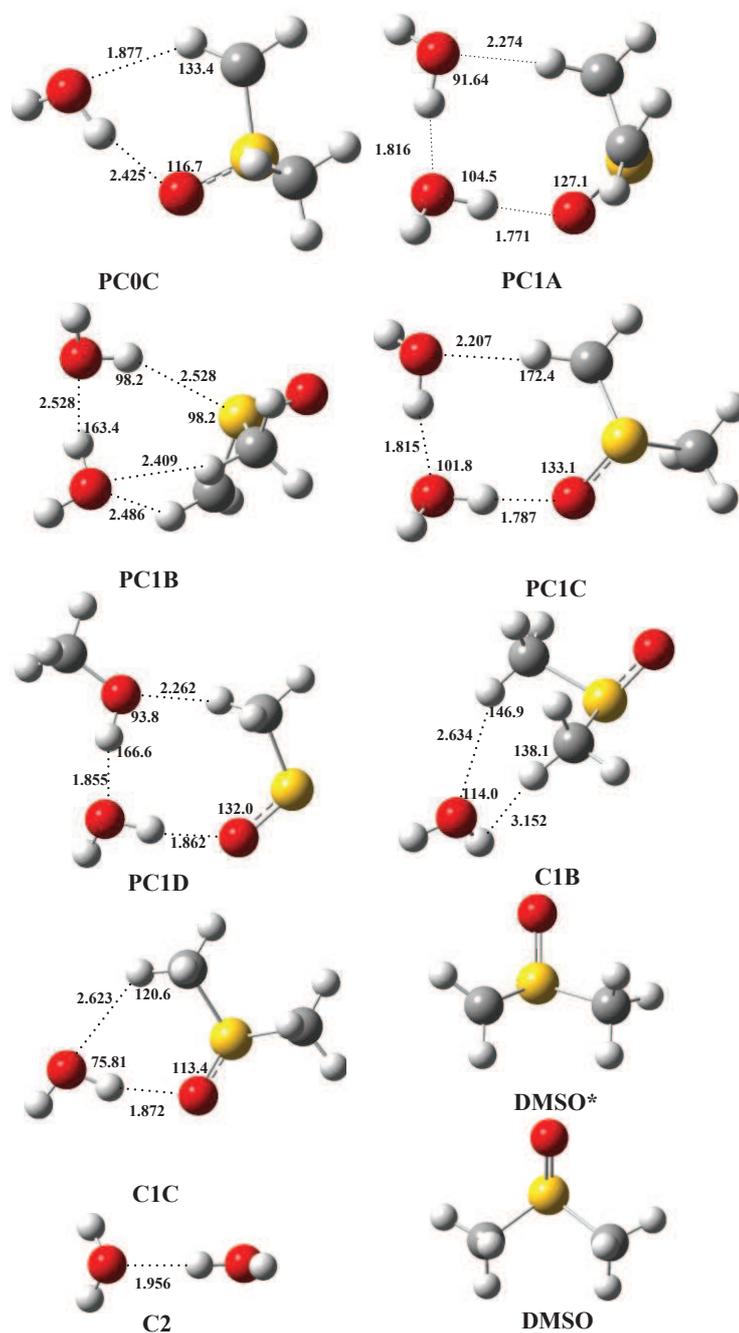
Figure 5: The optimized complexes and products at the b3lyp/aug-cc-pvtz level level of theory.

importance of these complexes is worth considering after the above analysis. It allow us to estimate the rate constant of path A, path B, path C, path D and path E with the temperature 298 K as listed in Table 3 and Table 4. It helps to estimate the effects of the single water molecule added and the kinetic is carried out in terms of the canonical transition state theory (CTST). The rate constant for path A and path B with water are increased as one water molecule added, even the path B with water is eight hundred times than that without water. The rate constant of SN2-type reaction (path D) is Almost no change ,for the results 7.18×10^{-33} cm^{3}molecule^{-1}s^{-1} with water and 9.49×10^{-33} cm^{3}molecule^{-1}s^{-1}. The rate constant of the S$\cdots$C bond breaking reaction (path E) without water is from 1.99×10^{-9} cm^{3}molecule^{-1}s^{-1} reduced to 8.61×10^{-10} cm^{3}molecule^{-1}s^{-1}. All are corresponding to the energy barriers information. When the energy barriers reduced as added one water molecule , the rate constant is increased.

4   Conclusions

The reactions of OH with dimethyl sulfoxide without and with water are employing high level theoretical methods and leads to the following conclusions:

(1) For this reaction we list five different kinds of elementary processes in this article. We have given the structures and energy of pre-reactive compounds , transition states and the release of the products . We also give the energy barrier for all the reaction. The results of the kinetic study for the naked reaction show a quite good agreement with the theory results from the literature.

(2) Water molecule can reduce the energy barriers in path A and path B. The energy barriers of path C, path D and path E is increased with the single water added.

(3) We have given the behavior of the rate constant respect to the temperature of 298 K which are proved that the water molecule can influence the reaction process. The rate constant is increased when one molecule added for path A and path B, instead, it is reduced as one water molecule adding for path C, path D and path E.

References

[1] J. M. Nicovich, S. Parthasarathy, and F. D. Pope, J. Phys. Chem. A 110 (2006) 6874.

[2] J. P. Putaud, B. M. Davison, S. F. Watts, N. Mihalopoulos, B. C. Nguyen, and C. N. Hewitt, Atmos. Environ. 33 (1999) 647.

[3] A. R. Bandy, D. C. Thornton, B. W. Blomquist, S. Chen, T. P. Wade, J. C. Ianni, G. M. Mitchell, and W. Nadler, Geophys. Res. Lett. 23 (1996) 741.

[4] H. Berresheim, J. W. Huey, R. P. Thorn, F. L. Eisele, D. J. Tanner, and A. Jefferson, J. Geophys. Res. 103 (1998)1629.

[5] J. Sciare, E. Baboukas, R. Hancy, N. Mihalopoulos, and B. C. Nguyen, J. Atmos. Chem. 30 (1998) 229.

[6] H. Bardouki, H. Berresheim, M. Vrekoussis, J. Sciare, G. Kouvarakis, K. Oikonomou, J. Schneider, and N. Mihalopoulos, Atmos. Chem. Phys. 3 (2003) 1871.

[7] T. Ingham, D. Bauer, R. Sander, P. J. Crutzen, and J. N. Crowley, J. Phys. Chem. A 103 (1999) 7199.

[8] G. P. Knight and J. N. Crowley, Phys. Chem. Chem. Phys. 3 (2001) 393.

[9] A. R. Ravishankara, Y. Rudich, R. Talukdar, S. B. Barone, Philos. Trans. R. Soc. London B 352 (1997) 171.

[10] J. E. Lovelock, R. J. Maggs, and R. A. Rasmussen, Nature 237 (1972) 452.

[11] N. González-García, Á. González-Lafont, and J. M. Lluch, J. Phys. Chem. A 110 (2006) 798.

[12] A. Gross, I. Barnes, R. M. Sørensen, J. Kongsted, and K. V. Mikkelsen, J. Phys. Chem. A 108 (2004) 8659.

[13] N. Yukio, G. Masashi, H. Satoshi, and K. Masahiro, J. Phys. Chem. A 105 (2001) 11045.

[14] M. O. Andreae, Marine Chem.30 (1990) 1.

[15] S. SØrensen, H. F. Hansen, M. Mangoni, J. Hjorth, and N. R. Jensen, J. Atmos. Chem. 24 (1996) 299.

[16] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. 100 (1996) 14703.

[17] B. Dmitri, K. Alexander, L. Gerard, and L. B. Georges, J. Phys. Chem. A 107 (2003) 1155.

[18] M. Pham, J. F. Müller, G. P. Brasseur, C. Granier, and G. Megie, J. Geophys. Res. 100 (1995) 26061.

[19] T. S. Bates, B. K. Lamb, A. Guenther, J. Dignon, and R. E. Stoiber, J. Atmos. Chem. 14 (1992) 315.

[20] P. A. Spiro, D. J. Jacob, and J. A. Logan, J. Geophys. Res. 97 (1992) 6023.

[21] J. Charlson, J. E. Lovelock, M. O. Andreae, and S. G. Warren, Nature 326 (1987) 655.

[22] I. Barnes, V. Bastian, K. H. Becker, and D. Martin, In: Biogenic Sulfur in the Environment. E. S. Saltzman and W. J. Cooper, eds. (American Chemical Society, Washington, DC, 1989) pp. 476-488.

[23] H. Falbe-Hansen, S. Sorensen, N. R. Jensen, T. Pedersen, Hjorth, J. Atmos. Environ. 34 (2000) 1543.

[24] I. Barnes, J. Hjorth, and N. Mihalopoulos, Chem. Rev. 106 (2006) 940.

[25] E. Martlnez, A. Aranda, Y. Dlaz de Mera, D. Rodrlguez, R. Lopez, and J. Albaladejo, Environ. Sci. Technol. 36 (2002) 1226.

[26] V. Solange and S. M. Resende, J. Phys. Chem. A 108 (2004) 2284.

[27] G. S. Tyndall and A. R. Ravishankara, Int. J. Chem. Kinet. 23 (1991) 483.

[28] S. Sekusak, P. Piecuch, R. J. Bartlett, and M. G .Cory, J. Phys. Chem. A 104 (2000) 8779.

[29] T. Uchimaru, S. Tsuzuki, M. Sugie, K. Tokuhashi, and A. Sekiya, Chem. Phys. 324 (2006) 465.

[30] F. M. Tao, K. Higgins, W. Klemperer, and D. D. Nelson, Geophys. Res. Lett. 23 (1996) 1797.

[31] S. P. Urbanski, R. E. Stickel, and P. H. Wine, J. Phys. Chem. A. 102 (1998)10522.

[32] A. J. Hynes and P. H. Wine, J. Atmos. Chem. 24 (1996) 23.

[33] S. B. Barone, A. A. Turnipseed, and A. R. Ravishankara, J. Phys. Chem. 100 (1996) 14694.

[34] A. J. Hynes, P. H. Wine, and D. H. Semmes, J. Phys. Chem. 90 (1986) 4148.

[35] P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. 85 (1981) 2660.

[36] C. Arsene, I. Barnes, K. H. Becker, and R. Mocanu, Atmos. Environ. 35 (2001) 3769.

[37] C. Arsene, I. Barnes, K. Becker, W. Schneider, T. Wallington, N. Mihalopoulos, and I. Patroescu-Klotz, Environ. Sci. Technol. 36 (2002) 5155.

[38] A. Kukui, D. Borissenko, G. Laverdet, and L. B. Georges, J. Phys. Chem. A 107 (2003) 5732.

[39] S. Jorgensen and H. G. Kjaergaard, J. Phys. Chem. A 114 (2010) 4857.

[40] L. Zhu, J. M. Nicovich, and P. H. Wine, Aquat. Sci. 65 (2003) 425.

[41] N. González-García, Á. González-Lafont, and J. M. Lluch, J. Comput. Chem. 26 (2005) 569.

[42] J. M. Ranirez-Anguita, A. G. Lez-Lafont, and J. M Lluch, J. Comput. Chem. 30 (2009) 1477.

[43] S. M. Vallina, R. Simo, S. Gasso, C. de Boyer-Montégut, E. del Río,E. Jurado, and J. Dachs, Global Biogeochemical Cycles. 21(2007) GB2004.

[44] N. González-García, Á. González-Lafont, and J. M.Lluch, Chem. Phys. Chem, 8 (2007) 255.

[45] S. Aloisio, Chem. Phys. 326 (2006) 335.

[46] L. Wang and J. Zhang, Chem. Phys. Lett. 356 (2002) 490.

[47] C. Iuga, J. R. Alvarez-Idaboy, and A. Vivier-Bunge, J. Phys. Chem. A 115 (2011) 5138.

[48] E. Vohringer-Martinez, B. Hansmann, H. Hernandez, J. S. Francisco, J. Troe, and B. Abel, Science 315 (2007) 497.

[49] D. de J. Medeiros and A. S. Pimentel, J. Phys. Chem. A 115 (2011) 6357.

[50] J. M. Anglada and J. Gonzalez, Chemphyschem. 10 (2009) 3034 .

[51] Y. Luo, S. Maeda, and K. Ohno, Chem. Phys. Lett. 469 (2009) 57.

[52] R. S. Zhu, and M. C. Lin, Chem. Phys. Lett. 354 (2002) 217.

[53] R. J. Buszek and J. S. Francisco, J. Phys. Chem. A 113 (2009) 5333.

[54]] E. Vöhringer-Martinez, E. Tellbach, M. Liessmann, and B. Abel, J. Phys. Chem. A 114 (2010) 9720.

[55] M. A. Allodi, M. E. Dunn, J. Livada, K. N. Kirschner, and G. C. Shields, J. Phys. Chem. A 110 (2006) 13283.

[56] J. Gonzalez and J. M. Anglada, J. Phys. Chem. A 114 (2010) 9151.

[57] B. Long, X. F. Tan, D. S. Ren, and W. J. Zhang, J. Mol. Struct.(Theochem.) 956 (2010) 44.

[58] B. Long, W. J. Zhang, X. F. Tan, Z. W. Long, Y. B. Wang, and D. S. Ren, J. Phys. Chem. A 115 (2011) 1350.

[59] B. Long, X. F. Tan, Z. W. Long, Y. B. Wang, D. S. Ren, and W. J. Zhang, J. Phys. Chem. A 115 (2011) 6559.

[60] J. Gonzalez, J. M. Anglada, R. J. Buszek, and J. S. Francisco, J. Am. Chem. Soc. 133 (2011) 3345.

[61] N. Butkovskaya, M. T. Rayez, J. C. Rayez, A. Kukui, and G. L. Bras, J. Phys. Chem. A 113 (2009) 11327.

[62] Y. X. Tang, G. S. Tyndall, and J. J. Orlando, J. Phys. Chem. A 114 (2010) 369.

[63] B. Long, W. J. Zhang, X. F. Tan, Z. W. Long, Y. B. Wang, and D. S. Ren, Comput. Theor. Chem. 964 (2011) 248.

[64] G. Frost and V. Vaida, J. Geophys. Res. 100 (1995)18803.

[65] F. M. Tao, K. Higgins, W. Klemperer, and D. D. Nel-son, Geophys. Res. Lett. 23(1996) 1797.

[66] E. J. Meijer and M. Sprik, J. Phys. Chem. A 102 (1998) 2893.

[67] C. Iuga, J. R. Alvarez-Idaboy, L. Reyes, and A. Vivier-Bunge, J. Phys. Chem. Lett. 1 (2010) 3112.

[68] V. Vaida and J. D. Simon, Science 268 (1995) 1443.

[69] M. J. Frisch, G. W. Trucks, and H. B. Schlegel, *et al.*, Gaussian 09, Rev. A 02 (Gaussian, Inc., Wallingford CT, 2009).