



Mechanistic and energetic study of the atmospheric reaction of hydrosulfinyl and mercapto radicals



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ABSTRACT

The gas phase reaction pathways of hydrosulfinyl, HSO, and mercapto, HS, have been studied computationally on the singlet potential energy surface. All species in the title reaction have been optimized using the MP2 method in connection with 6-311++G(3df,3pd) basis set. The single point energy calculations at the CCSD(T) level have been carried out on the optimized geometries of the MP2 computational level using aug-cc-pVTZ basis set. Five types of products, $\text{H}_2\text{S} + {}^3\text{SO}$, $\text{S}_2\text{O} + \text{H}_2$, $\text{H}_2\text{O} + {}^3\text{S}_2$, trans-HSSOH and trans-HSOSH, are formed from HSO and HS reaction. trans-HSOSH adduct is directly generated from the reactants after passing two transition states. Other products have been obtained through changing the singlet reactant complex defined as CR. All products have enough stability in thermodynamic approach. trans-HSSOH and $\text{H}_2\text{O} + {}^3\text{S}_2$ products with higher stability are defined as thermodynamic products. The kinetic investigations show that the trans-HSOSH adducts is obtained as the main product. Also, the rate constants show a non-Arrhenius behavior in the temperature range of 300–2500 K.

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1. Introduction

The study and development of challenge of the atmospheric oxidation are of fundamental importance in modeling the global sulfur cycle [1], since it provides efficient solutions for critical problems encountered in many scientific items of equipment. However, the accurate determinations of kinetic and mechanism of its oxidation reaction under atmospheric conditions are a challenge. There are different suggestions to conquer this challenge and among them, high accuracy quantum chemical methods have played their role into resolve this challenge. Newly, quantum kinetic was correctly depended on the use of inexpensive personal computers and in various cases supercomputers. For obtain to efficiently kinetic and thermodynamic information of a reaction, it is essential to have an understanding of potential energy surfaces (PESs) as it relate to chemical structure and how it link structure to the various properties of interest [2].

Sulfur compounds play as crucial role in polluting the human beings' survival surrounding [3]. They are involved in different significance processes such as the development of acid rain, or ozone depletion. A detailed knowledge of their ruin mechanism is of massive interest in understanding the chemistry of the troposphere [4–6].

The hydrosulfinyl radical, HSO, is of great importance and interest in the Earth's atmosphere [7–13]. Because of it makes the main contribution to the oxidation of H_2S and plays an important role in the $\text{H}_2\text{S} + \text{O}_2$ reaction as an intermediate [14]. However, it was estimated as the reaction intermediate in the $\text{H}_2\text{S} + \text{O}_3$ [15]. The case of HSO, which is known to play an essential role in the reaction kinetics of sulfur-containing compounds, is a characteristic example [16]. So, in the last 30 years several experimental and theoretical studies have been performed to characterize the structure and properties of HSO [17], spectroscopy of HSO radical [8,18], estimation of the heat of formation for HSO [1,16] and of the HSO–SOH isomerization energy [19].

The chemistry of HSO is not well recognized; few investigations of reactions of HSO with O_3 [13,20] O_2 and NO_2 [21] have been reported. Although the reaction of HSO with some molecules such as molecular oxygen has been investigated and reported in the literature, no analogous study with atomic oxygen has, to our knowledge, been published [22]. However, the reaction of HSO and ozone take place in the troposphere and stratosphere [16]. Hence, a number of theoretical and experimental studies of the HSO radical have been reported so far [8]. Experimental studies have been revealed that HSO can catalytically destroy ozone according to the following scheme [6].



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According to the literature, if at the low temperatures of the stratosphere, HSO can react with ozone to regenerate HS: [23]



In order for reaction (2) to be exothermic, the enthalpy of formation of HSO must be less than -2.1 ± 1.6 kcal/mol [19].

Moreover, there are some reports demonstrated that the HSO radical has been generated as a product in the reaction between HS and NO_2 , according to the following:



Notable that, this reaction, Eq. (3), can achieve comparable levels in polluted air where the concentration of NO_2 is major (>40 ppm) [20].

The kinetic point of view, the rate constant of the formation of HSO via reactions (1) and (3) estimated about $k_{298} = 3.5 \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$ and 7×10^{-11} cm^3 molecule $^{-1}$ s $^{-1}$, respectively [16].

There are a few kinetic studies of the HSO reaction. Because of the HS is a commonly used pioneer for HSO, it has been suggested that the kinetics of the HSO radical are closely related to those of HS [24].

In our knowledge, the reaction mechanism of HSO with HS is unclear and the main channels of producing $\text{H}_2\text{O} + {}^3\text{S}_2$ and HSSOH have not been experimentally or theoretically identified. The goal of the present work is the computational study of the mechanisms of HSO + HS reaction to identify some final products and their production pathways. Also, the particular emphasis has been placed on the study of the potential energy surfaces, PESs, of the above reaction. Also, special notice has been given to the thermodynamics aspect of the reaction. We also carry out a complete analysis of the singlet potential energy surface of the reaction. All minima and transition states are characterized on all the pathways. Also, different stable products such as $\text{H}_2\text{O} + {}^3\text{S}_2$ and some other products with low stability such as $\text{H}_2\text{S} + {}^3\text{SO}$, $\text{S}_2\text{O} + \text{H}_2$, trans-HSSOH and trans-HSOSH have been identified in this article. The kinetic investigations show that the trans-HSOSH adduct is found as the main product.

2. Computational method

At first, we have been fully optimized the geometries of all species on the title reaction mechanism to find minima on the potential energy surface using second-order Møller–Plesset perturbation theory [25] in conjunction with 6-311++G(3df,3pd) [26] basis set and also G3MP2 [27] level of computation. To determine the nature of the corresponding stationary point, the vibrational frequencies are obtained in these levels of the treatment. Any transition state characterizes via a single imaginary frequency and any intermediate has all real frequencies. Also, vibrational frequency calculations have been done to provide the zero-point energies correction, ZPE, and thermodynamic parameters.

To obtain more reliable energies, the single points energy calculations have been done at the CCSD(T) [28–31] level on the all optimized geometries at the MP2/6-311++G(3df,3pd) level using aug-cc-pVTZ [32,33] basis set. Because of the reactants are doublet states and ${}^3\text{S}_2$, ${}^3\text{SO}$ as final adducts are triplet states, we have checked these species for spin contamination error. Results show the maximum deviation among obtained and theoretical eigenvalues in S^2 is 4.3%. So, our suggested species don't have any spin contamination problem. The values of the T1 diagnostic [34] of the CCSD(T) wave function are obtained with the aim of check the multi-reference character of the wave function and reliability of single-determinant-based methods. Obtained results for T1 diagnostic indicate that the chosen methods for geometry optimization, MP2 and G3MP2, have enough accuracy in this work.

Intrinsic reaction coordinate, IRC, [35] analysis are used for confirming of the transition states attach correctly the reactants to the correspondent products. Moreover, the basis set superposition errors (BSSE) [36] carried out to gain a better estimation of the relative stability of different complexes at the CCSD(T) method. The computed values for BSSE energy show that the selected method and basis set have enough accuracy.

The bonding features have been investigated for some stationary points of interest molecule by using the atoms in molecules, AIM, analysis [37,38]. All the calculations are done with the GAUSSIAN 03 program [39].

3. Results and discussion

In this work, the reaction pathways begin with the formation of one collision complex as defined CR. Other intermediates are designated by the prefix IN and a number to differentiate from each other. Product complexes are shown with CP and a number that are found at the end of channels before final products. CR and CP differs with the corresponding reactants and products due to the existence of at least one van der Waals interaction among the reactants or products. The transition states are labeled by TS and followed a number. The optimized geometries of the reactants, intermediates, transition states and products involved in the title reaction at the MP2 level of computation are presented in Fig. 1 and their Cartesian coordinate available in the supporting information. Reaction pathways for different adducts in the singlet potential energy surfaces, PES, are plotted in Figs. 2–4 at the MP2 method. To simplify our discussions, the energy of the reactants, HSO + HS, is set to zero for reference.

The total energies, relative energies, ZPE and BSSE energies of all species involved in the reaction have been tabulated in Table 1 for the MP2, G3MP2 and CCSD(T) levels of computations. Also, T1 diagnostic are collected in Table 1. T1 diagnostic results confirm the selected computational methods are enough accurate. Table 2 contains the imaginary frequencies of transition states, thermodynamics data of step reactions and barrier energies of transition state in comparison with the corresponding complex on the singlet potential energy surface at the MP2 method. Vibrational frequencies of all species are summarized in the Supplementary Data (Table S1). Thermodynamic data of overall reaction are shown in Table 3. The topological data of selected stationary points are summarized in Table 4. Table 5 contains the structural parameters for the HSO radical in this work and numerous levels of theory that reported in some Ref. [5,9,10,12,14,19,52]. The geometrical parameters in the present work are compared with various levels of theories and experimental values. Obtained results show that the structural parameters of HSO in the present study are in good agreement with experimental data by Ohashi et al. [40]. Also, the calculated vibrational frequencies for the HSO radical and HSSOH in some levels of theories and experimental results are listed in Table 6. [9,14,19,21,40,41,45]. Finally, the rate constant for the kinetic favor pathway is displayed in Table 7 and also, Arrhenius plot for this pathway is plotted in Fig. 5.

3.1. Initial connection

The most of observed complexity on the energy profile (in Figs. 2–4) is obtained of the transformation of one minima that is founded in the singlet PES as initial connection. It has been designated as CR. The geometry of this complex is shown in Fig. 1. Its molecular symmetry is C1. The pre-reactive complex CR is formed when the sulfur atoms of HSO and HS fragments reach to each other without entrancing any barrier energy. The length of newly formed bond between two sulfur atoms in CR is 2.118 Å at the

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