Theoretical study on the mechanism and thermodynamic of methanethiol and ozone reaction

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ABSTRACT

Reaction mechanism of methanethiol oxidation with ozone are carried out using the B3LYP and CCSD(T) theoretical approaches in connection with the 6-311++G(3df,3pd) basis set. Results confirm six kinds of products, P1–P6, which have enough thermodynamic stability. In thermodynamic viewpoint, the P6 product is the most favored adduct of the $CH_3SH + O_3$ gas phase reaction at atmospheric pressure and 298.15 K temperature. The P6 adduct, $CH_3OH + SO_2$, is spontaneous and exothermic with −146.47 and −146.81 kcal/mol in Gibbs free energy and enthalpy of reaction at the B3LYP level, respectively. In kinetic viewpoint, the $CH_2S + H_2O_2 + O_2$, P2 adduct, as final product after passing two transition state low level is the most favorite path.

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1. Introduction

Organic sulfide compounds play an important role in tropospheric chemistry. Thiols are highly reactive sulfur-containing species well known for their disagreeable odors. The most volatile of thiols is methanethiol (also known as methyl mercaptan), which is one of the natural sources of sulfur compounds emitted into the atmosphere. Due to the extremely low odor threshold of methanethiol, it is added to natural gas, enabling people to detect leaks by smell. Methanethiol is the most simple and important atmospheric sulfide which is commonly known to cause serious environmental and human health problems [1]. It is also a colorless weak acid, found in the blood and brain of humans and other animal as well as planet tissues. At very high concentration it is highly toxic and affects the central nervous system [2].

Methanethiol (CH_3SH) is one of the most important products of degradation of organic matter, it is released from decaying organic matter in marshes and it is present in coal tar and some crude oils [3]. In addition, colonic bacteria produce large quantities of the highly methanethiol [4].

In anoxic freshwater sediments dimethyl sulfide and methanethiol are generally considered to be the dominant volatile organic sulfur compounds. Fluxes of methanethiol from freshwater systems toward the atmosphere depend on the steady-state concentration of the balance between its formation and degradations. It is used as an additive and odorant in the light hydrocarbon streams such as refinery gas and in fuels including natural gas in the United States and Europe. Methyl mercaptan is one of the natural sources of sulfur emitted into the atmosphere. So, the process of removal of methane thiol is of great scientific and practical importance [1].

$CH_3OH–H_2S$ route for the synthesis of methanethiol is an inefficient process, which proceeds via a methane steam reforming to syngas ($CO + H_2$) and the synthesis of methanol from syngas. Methanethiol, CH_3SH, is very active and can be used an important intermediate in the production of organosulfur compounds, pesticide, medicine and synthetic material [5]. However, it is mainly used to produce methionine, which use as a dietary component in poultry and animal feed. Methanethiol is also used in the plastics industry and as a precursor in the manufacture of pesticides.

Oxidation reactions of organic sulfides are of great importance in biological systems [6,7], both in the atmosphere [8] and on surfaces [9]. The gas phase oxidation of organic sulfur compounds has become of increasing importance in relation with pollution by SO_2 and tropospheric and stratospheric sulfur containing aerosols [10] methanethiol is interesting in view of its presence in the Earth's atmosphere. It can further be used as an important intermediate in the production of organosulfur compounds, such as dimethyl sulfoxide, and dimethyl sulfone [11].

The oxidation of CH_3SH ultimately leads to the formation of SO_2 and results in the formation and growth of sulfate aerosols, which are the main sources of cloud-condensation nuclei, removed by highly acidic precipitation [12]. CH_3SH has been removed from the stream by catalytic incineration [13], chemisorptions [14], and packed tower scrubbing [15].

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So far, related experimental and theoretical studies with the present study, such as on CH_3SH with OH, HO_2, NO_3, and Cl reactions have been done in the gas phase. Particularly, the reaction of CH_3SH with OH has been the subject of numerous kinetic studies. Atkinson et al. studied the $CH_3SH + OH$ reaction in argon by the flash photolysis technique at 50–100 Torr, and obtained an Arrhenius expression of $k = 8.89 \times 10^{-12} \exp[(398 + 151)/T]$ cm^3 molecule^{-1} s^{-1} [16]. Wine et al. used very similar conditions and the same technique, that obtained the expression $k = 1.15 \times 10^{-11} \exp[(338 + 100)/T]$ cm^3 molecule^{-1} s^{-1} [17]. In later studies, Wine and co-workers attempted to elucidate mechanistic details of the reaction [18,19]. Another competitive rate study by Barnes et al. produced a rate constant of $k_{298} = (3.6 + 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, in agreement with the flash photolysis studies [20]. Based upon a least-squares analysis of the absolute rate coefficients of Atkinson et al. [16], Wine et al. [17,19] and Hynes and Wine [18] become $k = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. In studies of $HO_2 + CH_3SH \rightarrow$ products reaction, Mellouki and Ravishankara has shown that the absolute rate coefficient is $k < 4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K [21]. Wallington et al. obtained $k = (8.1 + 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for $NO_3 + CH_3SH$ reaction [22].

The sulfur atom can bind to one or more oxygen and hydrogen atoms, or hydrogen atoms can absorbed with oxygen atoms of the ozone molecules, and carbon can bind to oxygen atom instead of sulfur.

Ozone is an important constituent of the atmosphere; its main role is preventing UV rays reaching the Earth's surface. The reaction of this material with gaseous compounds is of high importance. The $CH_3SH + O_3$ reaction mechanism has been studied in this letter by means of computational methods based on quantum theory, characterizing all the minima and transition states on all pathways. The results obtained have allowed us to compare the likelihood of each way in order to determine which reaction pathway is energetically and kinetically favored.

In spite of slow reaction rates, the thermodynamic stability of products such as SO_2 and methanol, and the atmospheric importance of adducts are our motivation for doing this investigation. So, the aim of the present work is analysis of the thermodynamic and kinetic aspects of the methanethiol and ozone oxidation reactions. The gas phase reaction are investigated and suggested the mechanism for formation of six possible products as $CH_3SHO + {}^3O_2$, $CH_2S + H_2O + {}^3O_2$, $CH_2SHOH + {}^3O_2$, $HCOSH + H_2O_2$, $CH_2SO_2 + H_2O$ and $CH_3OH + SO_2$. Some of these products are produced from one reaction path, but some derive from two or more paths.

2. Computational method

All the calculations are performed with the Gaussian 03 program [23]. In the first step all the geometry optimizations were carried out using density functional theory (DFT) B3LYP [24] with the 6-311++G(3df-3pd) basis set [25]. All the obtained total energies were corrected with the zero point energy. To compute accurate relative energies, calculations are carried out at the CCSD(T) [26] method. In the above calculations, we report the T1 diagnostic values, which give a qualitative assessment of the significance of nondynamical correlation [27]. In order to obtain the total energies, the CCSD(T) energies are corrected with the zero point vibrational energy estimated by B3LYP/6-311++G(3df,3pd) calculations. The CCSD(T) have been employed for refining the electronic energies of the optimized structures. Total and relative energies of all species in the reaction were derived from B3LYP and CCSD(T) levels. Connection between reactants, intermediates, transition states, and products are confirmed by the intrinsic reaction coordinate (IRC) [27,28] method. The IRC method has been used to describe

minimum energy paths from transition state structures to the corresponding minima at the B3LYP level. Thermodynamic data for reactions are calculated at the B3LYP level. We computed the vibrational frequencies for the verification of the optimized geometries. Any reactant, product, and intermediate possess all real frequencies and all transition states have exactly one imaginary frequency. In addition, to confirm the optimized structures of all species and their atomic connectivity, the topological analyses of atoms in molecules (AIM) [29] were carried out by means of the AIM 2000 series of programs [30]. All these calculations are done at a temperature of 298.15 K and under atmospheric pressure.

3. Results and discussion

All the elementary reactions of methanethiol and ozone begins with the formation of a quasi-bound complex (C1–C4), followed by formation of a transition state (TS1–TS9) and some intermediates (IN1–IN7). In the exit channels, complex formation does also occur before the reaction products are formed these are labeled CP1–CP6. The optimized geometries for the $CH_3SH + O_3$ reaction at the B3LYP level are shown in Fig. 1. In Table 1, the total energies are given for the B3LYP and CCSD(T) levels and corresponding relative energies in comparison with the original reactants. In addition, T1 diagnostic in the CCSD(T) of all species are tabulated in Table 1. In this work, the stabilization energy is defined as the energy difference between the pre-reactive complex and the reactants. The energy difference between the transition state structure and the pre-reactive complex is denoted as the activation barrier. The reaction energy is the energy difference between the products and the reactants. To simplify our discussion, the energy of reactants, R ($CH_3SH + O_3$), is set to be zero for reference. Figs. 2 and 3 schematically display the energetic profiles for $CH_3SH + O_3$ reaction at the CCSD(T) level. Fig. 2, shows the reaction pathways for production of P1–P4 and Fig. 3 schematize the reaction pathways for the P5–P6 products. The calculated vibrational frequencies at the B3LYP level are listed in Table 1S in Supplementary data. All intermediate, INs, and pre-reactive complex, Cs, are true minima on the reaction PES and transition state, TS, has only one imaginary frequency. Table 2 gives the reaction internal energies, enthalpies, Gibbs free energies, and entropies at room temperature. The overall rate constant (in cm^3 molecule^{-1} s^{-1}) for P2 in the temperature range of 200–1000 K at the B3LYP/6-311++G(3df,3pd) has been calculated in Table 3. Finally, Fig. 4 shows an Arrhenius curves for the reaction rate constant k_T for P2 production of $CH_3SH + O_3$ reaction.

3.1. Reactants and initial complex formations

Four pre-reactive complexes are found when the original reactants approach to each other as C1, C2, C3 and C4. Pre-reactive complex C1 is formed when the terminal oxygen atom of molecular ozone approaches to the H4 hydrogen atom of methanethiol and the central oxygen atom of O_3 reacts with the sulfur atom of methanethiol. The interaction of H4 of methanethiol with a lone pair of terminal oxygen atom of O_3 in one side and interaction of O2 atom with a lone pair of sulfur atom of methanethiol in other side, leads to the formation of a five-membered ring complex, which named C1. The newly bonds formation in C1, H4–O3 and S8–O2, lengths are 2.391, and 3.310 Å, respectively. Hence, one of newly bonds formation (H4–O3) in C1 is a hydrogen bond. The bond length of O2–O3 in C1 is 1.257 Å longer than the corresponding bond in ozone, which corresponds to a relative increase of 5% at the B3LYP level. The formations of newly bonds are confirmed by an AIM topological analysis of wave function. This analysis reveals the presence of bond critical points (bcp), located between S8 and