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Theoretical study of the auto-catalyzed hydrolysis reaction of sulfur dioxide

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ABSTRACT

The hydrolysis reaction of sulfur dioxide (SO_2) to form sulfurous acid involving additional sulfurous acid (H_2SO_3) was investigated using high-level computational methods. With H_2SO_3, the reaction takes place via a double proton transfer process with a cage-like structure, which is different from the planar ring structure involved in a corresponding process with an additional water molecule (served as a catalyst). Our results show that H_2SO_3 is a better catalyst than water, as the barrier height for the H_2SO_3-catalyzed reaction is only 5.5 kcal/mol, compared to over 25.0 and 15.0 kcal/mol for the reaction without a catalyst and the H_2O-catalyzed reaction, respectively. In addition, the sulfurous acid dimer from the H_2SO_3-catalyzed reaction is more stable than hydrated H_2SO_3 from the H_2O-catalyzed reaction. Considering the existence of sulfurous acid in the aqueous phase and acidic aerosols, as well as the importance of SO_2 and H_2O in the atmosphere, our results will have potentially significant implications on the homogeneous and heterogeneous nucleation processes.

1. Introduction

Sulfur dioxide is one of the most important atmospheric pollutants, which is mainly from volcano eruption and the burning of fossil fuels [1]. The reactions of SO_2 in the atmosphere contribute to various environmental issues, including acid rain, formation of sulfate aerosols, and production of secondary organic aerosols [2]. As a result, substantial efforts have been dedicated to the understanding of the chemical processes of SO_2 in the atmosphere [3–9]. A critical step in many atmospheric processes is the adsorption of SO_2 on the gas–liquid surface [10–13]. However, the chemical mechanism for the subsequent reactions of SO_2 after adsorption is still poorly understood. The high solubility in water leads to the "wet" deposition of SO_2, in which the hydrolysis reaction plays a major role. The hydrolysis reaction of SO_2 in the atmosphere has a profound impact on the environment. The reaction contributes to the production of hygroscopic species which will act as seed molecules for aerosol formation [9]. In view of this, the sulfurous acid product may serve as either a donor or an acceptor of hydrogen bond, and thus provide as a precursor capable of oligomers and ultimately condense into atmospheric aerosols [14,15]. The hydrolysis reaction of SO_2 is kinetically and thermodynamically unfavorable in the gas phase [16,17], and the complete process has been poorly understood for the past decades.

In the hydrolysis reaction of SO_2, an additional water molecule may act as a proton transmitter or serve as a micro solvent, effectively reducing the energy barrier of reaction [18]. Recent efforts have been devoted to finding other species with similar effects in promoting the hydrolysis reaction of SO_2. Ammonia, an important ingredient of atmospheric aerosols, has been identified as a better proton transmitter than water in promoting the hydrolysis reaction of SO_2 [9]. More specifically, recent computational studies on the hydrolysis reactions of sulfur trioxide [19] and glyoxal [20], for example, suggested that atmospheric acid can dramatically lower the energy barriers of the hydrolysis reactions. Acid catalysis may also be important in the hydrolysis reaction of SO_2.

The solution of SO_2 is comprised of hydrated SO_2, sulfurous acid (H_2SO_3), and sulfonate ion (HSO_3^-) [6,11,14]. As a hydrolysis product, sulfurous acid is also expected to be contained in the acidic aerosols [14]. The characterization and isolation of H_2SO_3 is still a challenge in inorganic chemistry due to the kinetic instability of sulfurous acid. However, H_2SO_3 has been successfully generated in a neutralization–reionization mass spectrometric experiment [21]. In addition, the solvated sulfurous acid H_2SO_3–$(H_2O)_5$ is predicted to be more stable than hydrated sulfur dioxide SO_2–$(H_2O)_6$ [6]. In addition, the half-life of H_2SO_3 is estimated to be 24 h at room temperature, and Voegele et al. suggested that the dimeric

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H_2SO_3 is thermodynamically more stable than isolated SO_2 and H_2O molecules at 77 K [22].

In the present work, the hydrolysis reaction of SO_2 in the presence of sulfurous acid is studied using theoretical computation. Our primary objective is to know whether or not H_2SO_3 could act as an auto-catalyst for the formation of itself. Our next objective is to understand any potential effects of this reaction on the characterization and isolation of H_2SO_3 in laboratory. Natural Bonding Orbital (NBO) analysis will be performed to evaluate the nature of the catalytic effect. Kinetic simulations will be conducted over the temperatures 200–320 K. Atmospheric implications of this study will be discussed, particularly on atmospheric aerosol formation and particulate growth.

2. Computational methods

Quantum chemical calculations were performed using Gaussian 09 suite of program [23]. Equilibrium geometries corresponding to all local minima and transition states were optimized using the popular B3LYP hybrid density functional method with the cc-pV(T+d)Z basis set. The B3LYP/cc-pV(T+d)Z method has shown to provide reliable results for reactions of hydration of sulfuric acid [24] and the hydrolysis reactions of sulfur trioxide, catalyzed by formic acid [25] and sulfuric acid [19], respectively. Intermolecular interactions, particularly hydrogen bonding, may play an important role in the catalytic effect of H_2SO_3 in the hydrolysis reaction of SO_2. Second-order Moller–Plesset perturbation method (MP2), which is known reliable in describing noncovalent interactions [26–29], was also employed to confirm the adequate treatment of intermolecular interactions. All molecular geometries at the stationary points were re-optimized using MP2/cc-pV(T+d)Z method. Harmonic vibrational frequencies were obtained to verify each equilibrium geometry either at a local minimum or at a first-order saddle point. Furthermore, intrinsic reaction coordinate (IRC) calculations were performed to confirm each transition state that connects the desired reactant and product. Using B3LYP equilibrium geometries, electronic energies were further refined by the single point energy calculations using coupled-cluster theory with single, double, and perturbative triple excitations, CCSD(T), in conjunction with the extrapolation to the complete basis set limit (CBS) from augmented cc-pVDZ and cc-pVTZ energies. The KiSThelP program [30] was used for the kinetic calculations.

3. Results and discussion

Figs. 1 and 2 present the equilibrium geometries involved in the H_2O- and H_2SO_3-catalyzed reactions from B3LYP/cc-pV(T+d)Z and MP2/cc-pV(T+d)Z calculations. It is clear that the geometric parameters from B3LYP calculations are in good agreement with those from MP2 calculations. Overall, the deviations between the two methods are within 0.04 Å in hydrogen-bond lengths and 2.1° in hydrogen-bond angles. The results confirm that B3LYP/cc-pV(T+d)Z method gives an adequate description of the hydrogen bonds for the systems considered in this work. For simplicity, only the B3LYP geometries will be quoted in the following discussions.

3.1. H_2O-catalyzed reaction

The catalytic effect of a single water molecule on the gaseous hydrolysis reaction of SO_2 was studied previously with quantum chemical methods [9,16,18]. In the present study, we recalculated the reaction with a single H_2O as the catalyst, as well as the reaction without a catalyst, in order to compare consistently with the new reactions to be considered in the study. The potential energy surface (PES) profiles for the naked reaction and for the reactions

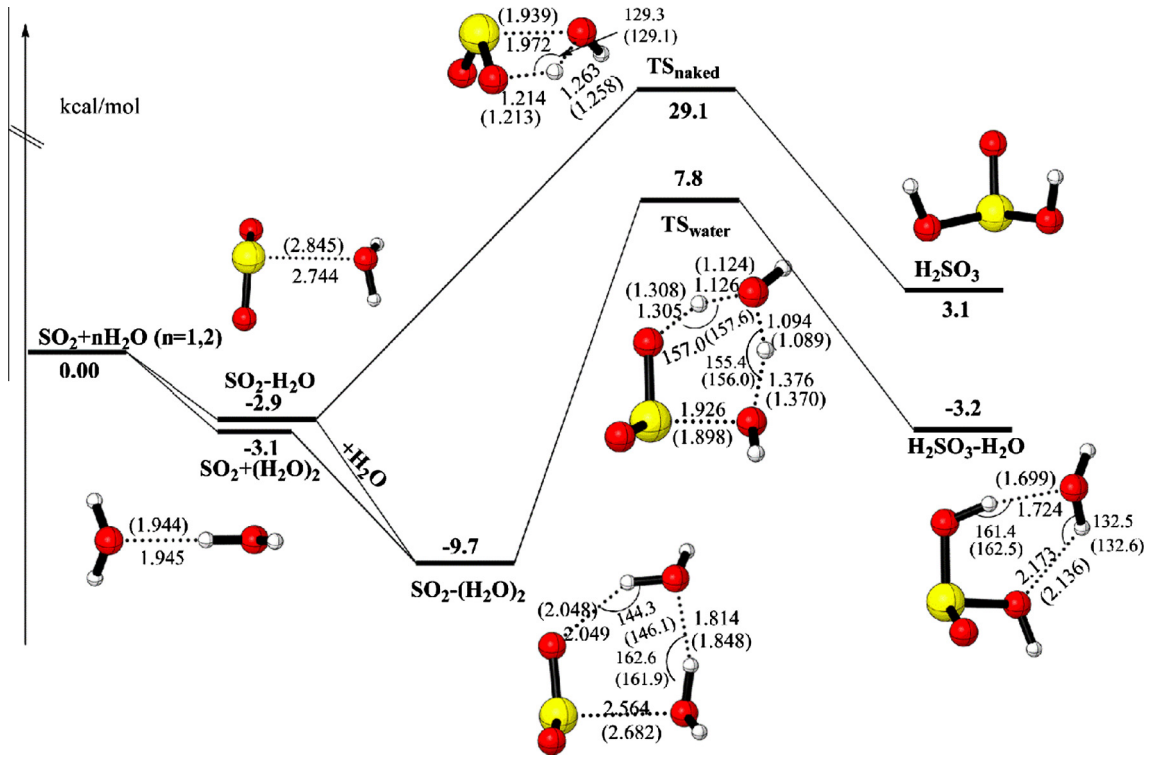

Fig. 1. Schematic potential energy surface for the $SO_2 + H_2O$, and $SO_2 + 2H_2O$ reactions. The corresponding geometries have been obtained at B3LYP/cc-pV(T+d)Z and MP2/cc-pV(T+d)Z (in brackets) level of theory. The energy profile has been calculated at the CCSD(T)/CBS//B3LYP/cc-pV(T+d)Z + ZPE level of theory (bond distances in angstrom, angles in degree).