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Catalytic effect of $(H_2O)_n$ (n = 1–2) on the hydrogen abstraction reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$ under tropospheric conditions

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ABSTRACT

The effects of $(H_2O)_n$ (n = 1–2) on hydrogen abstraction reaction ($H_2O_2 + HS \rightarrow H_2S + HO_2$) have been investigated at the level of theories of B3LYP and CCSD(T). The aug-cc-pVTZ basis set has been used in the present treatment. The catalytic effect has been found to be small for water dimer and is significant for water, because the effective rate constant for the water-catalyzed reaction being 3–4 orders of magnitude larger than the corresponding water-dimer assisted reaction. Compared to the un-catalyzed reaction, the rate enhancement due to water catalysis at lower temperature (e.g., 240 K) was only 0.17%, which was increased to 72.7% at higher temperature (e.g., 325 K).

1. Introduction

H_2O_2 is an important oxidant in the atmosphere [1], and the atmospheric chemistry of H_2O_2 is of central importance to explore the oxidizing capacity of the atmosphere. Production of H_2O_2 occurs primarily via the self-reaction of HO_2 radicals in the gas phase [2–4], while loss of H_2O_2 occurs primarily via photolysis and reaction with OH radical [5], and other species, such as Cl radical [6,7], ClO radical [8], NO_x [9,10], HS radical [11], Br radical [12] and HO_2 radical [13]. The HS radical plays an important role as an intermediate during thermal processing of coal in sulfur transformation and also an effective intermediate in the atmospheric chemistry of hydrogen sulfide [14]. It has been reported that all HS oxidized to either SO_2 or SO_3 finally contributes to acid rain [11,15–21]. Thus, the gas-phase reaction of H_2O_2 + HS is very helpful for the comprehending sulfur cycle in the atmosphere.

Experimentally, Friedl et al. [11] using discharge flow laser-induced fluorescence-resonance fluorescence technique measured the rate constant of H_2O_2 + HS reaction at 298 K at low pressure (1–8 torr of He) which is $<5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. However, the mechanism of H_2O_2 + HS reaction is still poorly understood theoretically. Therefore, in this study, the hydrogen abstraction mechanism for $H_2O_2 + HS \rightarrow H_2S + HO_2$ reaction has been investigated at CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory. The rate constant has been evaluated. The experimental and theoretical investigations discussed above provide meaningful information's about the mechanisms and kinetics of the H_2O_2 + HS reaction under tropospheric conditions. However, these efforts only focused on non-catalytic process of H_2O_2 + HS reaction.

In fact, the impact of water on the processes those occurring in the earth's atmosphere is significant [22,23]. The active role of water which is used as a catalyst [5,29–37] in the atmospheric reactions can form hydrogen-bonded complexes with atmospheric species such as ozone [24,25], nitrogen acid [26], sulphuric acid [27], OH radical [28], etc. and change their photo-chemical features. For instance, water forms hydrogen-bonded complexes ($H_2O\cdots HO_2$) with HO_2 radical [24,36–39]. The rate constant of the reaction of $H_2O\cdots HO_2$ complex with HO_2 radical enhances by 74 times due to HO_2 radicals self-reaction, which produces H_2O_2 and O_2 [4,39–41]. Because of the similar hydrogen bonding characteristics of $H_2O\cdots HO_2$ complex, the $H_2O_2\cdots H_2O$ complex has also been studied theoretically [5], and this has led to the recent studies to investigate the effects of water on hydrogen abstraction reactions of H_2O_2 with OH radical reported by Buszek et al. [5]. Moreover, some reports [5,42–44] have been demonstrated that how water molecule catalyzes radical-molecule reactions involving OH radical. The similarity in structures and properties between OH and HS radicals leads to the later one to form similar hydrogen bonding characteristics of $HO\cdots H_2O$ complex. These phenomena encourage us to model a gas-phase reaction of $H_2O\cdots H_2O_2\cdots HS$ ternary system, in which water is used as a catalyst. Thus, based on the hydrogen abstraction reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$

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without water, we herein report water-catalyzed $H_2O_2 + HS \rightarrow H_2S + HO_2$ reaction to determine if water-catalyzed processes can kinetically compete with non-catalytic processes in the gas-phase. Meanwhile, it is of interest to known whether water dimer will effect the $H_2O_2 + HS$ reaction as the concentration of water dimer [24,45,46] is up to 9×10^{14} molecules cm^{-3} [47,48] at 298 K.

In the present study, a detailed effects of $(H_2O)_n$ (n = 1–2) on the hydrogen abstraction reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$ have been carried out at CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory, which is organized as follows: firstly, the hydrogen abstraction reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$ is investigated to compare with $(H_2O)_n$-assisted processes. In what follows, the reactions of $H_2O\cdots H_2O_2 + HS$, $HS\cdots H_2O + H_2O_2$ and $H_2O\cdots HS + H_2O_2$ with a water molecule are evaluated by investigating direct hydrogen abstraction process and double hydrogen transfer mechanism. Then, direct hydrogen abstraction processes of $HS + (H_2O)_2\cdots H_2O_2$ and $H_2O_2 + (H_2O)_2\cdots HS$ with $(H_2O)_2$ are calculated. Finally, rate constants of the hydrogen abstraction reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$ with$(H_2O)_n$ are calculated to investigate the atmospheric relevance of the effect of $(H_2O)_n$. Overall, this work may lead to a better understanding of the effects of $(H_2O)_n$ on gas-phase reactions under tropospheric conditions.

2. Computational methods

The electronic structure calculations have been performed using Gaussian09 program package [49]. The geometries of all the reactants, the intermediate, transition states and products have been optimized at B3LYP/aug-cc-pVTZ level of theory. And the frequency analysis was performed to study the stationary point as well as the transition states. Moreover, the minimum energy path (MEP) has been achieved by the intrinsic reaction coordinate (IRC) [50–52] theory with a gradient step size of 0.01–0.05 $(amu)^{1/2}$bohr to confirm that the TS connects to minima along the reaction path. To obtain more reliable energy information, single-point energy calculations for the stationary points are carried out at the CCSD (T) method [53] in conjunction with aug-cc-pVTZ basis set that is based on the B3LYP/aug-cc-pVTZ -optimized geometries.

To estimate the effect of $(H_2O)_n$ (n = 1–2) added, the kinetic properties of the system were calculated using conventional transition state theory (TST) [54–56] with the Winger tunneling correction in the VKLab program [57] coupled with the steady state approximation. As described in Eq. (1), the title reaction without and with $(H_2O)_n$ all began with the formation of intermediate before progressing through the transition state.

$$\left.\begin{array}{l} H_2O_2 + HS \\ H_2O\cdots H_2O_2 + HS \\ HS\cdots H_2O + H_2O_2 \\ H_2O\cdots HS + H_2O_2 \\ (H_2O)_2\cdots H_2O_2 + HS \\ HS\cdots(H_2O)_2 + H_2O_2 \end{array}\right\} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{intermediate} \xrightarrow{k_2} \text{products} \tag{1}$$

Assuming that the intermediate was in equilibrium with the reactants and was at steady state [58], the overall rate constant was expressed as

$$k = \frac{k_1}{k_{-1} + k_2} k_2 \tag{2}$$

If $k_2 \ll k_{-1}$, the rate constant was rewritten as

$$k = \frac{k_1}{k_{-1} + k_2} k_2 = K_{eq} k_2 \tag{3}$$

where K_{eq} and k_2 were given by Eq. (4) and the VKLab program [57], respectively.

$$K_{eq}(T) = \sigma \frac{Q_{IM}}{Q_{R1} Q_{R2}} \exp\left(\frac{E_R - E_{IM}}{RT}\right) \tag{4}$$

In Eq. (4), the various Q values denote the partition functions of the intermediate, reactants R1 and R2, respectively. All partition functions are obtained using the B3LYP/aug-cc-pVTZ method. E_R, E_{CR} stand for the total energies of the reactants and intermediate, respectively; σ is the symmetry factor.

3. Results and discussions

3.1. Potential energy surfaces for $H_2O_2 + HS \rightarrow H_2S + HO_2$ reaction

For the hydrogen abstraction reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$, as depicted in Fig. 1, two elementary reaction paths were identified, depending on how the HS radical approached H_2O_2, corresponding to the *cis*- and *trans* orientations of the H_2O_2 and HS radical moieties. As seen in Fig. 1, a weak hydrogen bond between the H atom of H_2O_2 and the S atom of HS radical (with a computed H···S bond distance of 2.52 and 2.47 Å at the B3LYP/aug-cc-pVTZ level of theory) was present in IM1 and IM1a, which likely explained why the relative energy of IM1 and IM1a to the reactants (H_2O_2 and SH radical), shown in Fig. 1 and Table 1, was only −0.9 and −1.7 kcal mol^{-1}. Starting from IM1 and IM1a, the S atom of HS radical attacked the H atom of H_2O_2 through the *cis*-transition state

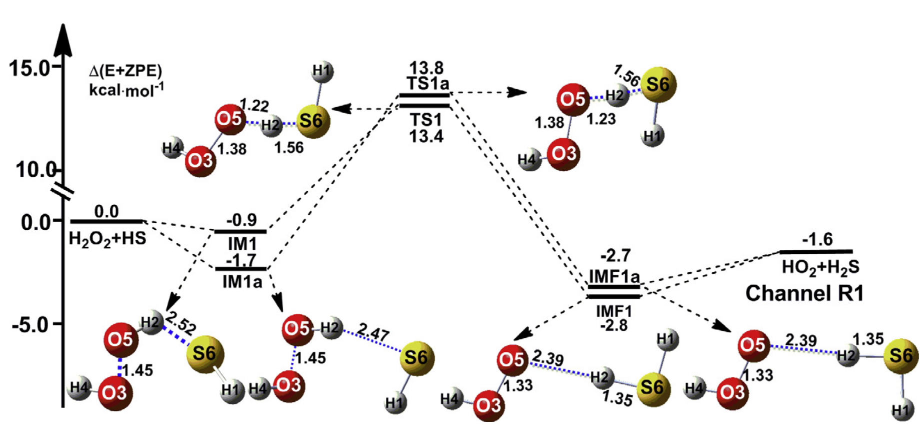

Fig. 1. Schematic energy diagram for the reaction of $H_2O_2 + HS \rightarrow H_2S + HO_2$; energies (kcal mol^{-1}) computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level include zero-point energy correction.