

Ab initio Study on the Complex Forming Reaction of OH and H₂O in the Gas Phase

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ABSTRACT

The estimation of the concentration of hydroxyl radical (OH) in the atmosphere is essential to build atmospheric models and to understand the mechanisms of the reactions involved in OH. Although water vapor is one of the most abundant species in the troposphere, only a few studies have been performed for the reaction of OH and water vapor. Here I demonstrate an *ab initio* study on the complex forming reaction of OH with H₂O in the gas phase performed based on density functional theory to calculate the reaction rate and the energy states of the reactant and the OH–H₂O complex. The structure of the complex, which belongs to the Cs point group, was optimized at global minima. The transition state was not found at the B3LYP and MP2 levels of theory. Rate constants of the forward and the reverse reactions were calculated as $1.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $5.3 \times 10^9 \text{ s}^{-1}$, respectively. The extremely slow rates of complex forming reaction and the resulting hydrogen atom exchange reaction of OH and H₂O, which are consistent with experimentally determined values, imply a negligible possibility of a change in OH reactivity through the title reaction.

Key words: OH radical, Water complex formation, *Ab initio* study, Reaction kinetics, Atmospheric chemistry, Chemical Ionization Mass Spectrometry

1. INTRODUCTION

The hydroxyl radical (OH) is involved in numerous oxidative reactions in the atmosphere. It initiates not only the oxidation of gaseous molecules, such as volatile organic compounds (VOCs), carbon monoxide

(CO), and ozone (O₃) (Seinfeld *et al.*, 1998), but is also involved in heterogeneous reactions on various surfaces of atmospheric importance, including aerosols of sea salt, soot, inorganic dust, and water (Park *et al.*, 2013, 2012, 2009, 2008; Molina *et al.*, 2004; Bertram *et al.*, 2001). Although such reactions with OH have been previously studied, field measurements have revealed consistent overestimation of OH concentrations in atmospheric models (Shirley *et al.*, 2006; Carslaw *et al.*, 1999; Mckeen *et al.*, 1997; Eisele *et al.*, 1994; Poppe *et al.*, 1994). Such discrepancies indicate the presence of OH sinks that are unaccounted for in most models. Therefore, additional reaction pathways and their kinetics are required to fully explain and understand the atmospheric OH budget.

Water vapor is one of the major components of the troposphere and can reach levels up to 4% by volume. Recent studies have revealed that adsorbed water on the surface of aerosols in the troposphere affects heterogeneous reactions between radicals and aerosol particles (Park *et al.*, 2008). Adsorbed water can also interfere with gaseous reactions in the troposphere by removing or blocking one or more of the reactants (Sennikov *et al.*, 2005; Hansen and Francisco, 2002; Aloisio and Francisco, 2000). Due to its ability to form hydrogen bonds, water vapor clusters readily with various gaseous species. For example, water dimers have been the focus of both experimental and theoretical studies (Kyke *et al.*, 1997; Feyereisen *et al.*, 1996; Newton and Kestner, 1983).

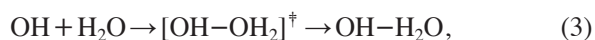
A water molecule can also form a complex with an OH radical (OH–H₂O). This complex acts as an intermediate in the hydrogen (H) atom transfer reaction between OH and H₂O.



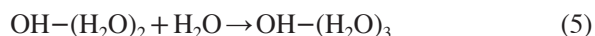
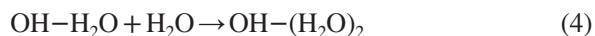
Experimental studies with isotope labeling of H atoms have shown that the above H atom transfer is extremely

slow with a rate constant of $(2.2 \pm 1.0) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature (Dubey *et al.*, 1997). The theoretical calculated rate constant for the same reaction has been reported as $1.67 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Uchimaru *et al.*, 2003). These studies focused on the H atom transfer between an OH radical and a water molecule, which results in no changes to the overall atmospheric OH concentration.

Conversely, complex formation between OH and H₂O molecules can serve as an OH sink in the atmosphere according to



where the double dagger indicates the transition state. In addition, further complexation with additional H₂O molecules, forming OH-(H₂O)_n, can occur when a single OH-H₂O complex meets another H₂O molecule before self-dissociation or isomerization according to



No clear experimental evidence corroborates for the existence of such a complex, although theoretical studies have estimated its structure and energy (Karakus and Ozkan, 2005; Sennikov *et al.*, 2005; Aloisio and Francisco, 2000; Wang *et al.*, 1999; Dubey *et al.*, 1997; Kim *et al.*, 1991). Little is known of the rate constant and mechanism of the complex forming reaction of OH and H₂O. A quantitative investigation of the aforementioned reaction rate would enable estimates regarding the contributions of the OH-H₂O complex to changes in OH reactivity that may account for the missing sink of OH in atmospheric models. Such a study would also enhance our fundamental knowledge of gas-phase reactions between radicals and molecules.

In this paper, a theoretical study of the complex forming reaction between a single OH radical and a H₂O molecule [Rxn. (1)] was presented. This study provides a means of estimating the rate and equilibrium constants based on a reactive hard-sphere model and the Eyring equation. *Ab initio* calculations were performed to optimize the geometries and energies of the reactants, the products, and the transition state. The study was then expanded to investigate multiple complexes of OH radicals and H₂O molecules, and of complexes of OH⁻ ions with H₂O molecules. This report provides information on the degree to which the formation of OH-H₂O complexes acts as an OH sink. The knowledge thus obtained can be applied to atmospheric models to account for changes in OH reactivity in the atmosphere. In addition, the possible origin of OH-H₂O complex ions in chemical ionization mass spectra obtained under humid conditions is discussed

with regard to reaction kinetics.

2. THEORETICAL METHODS

Ab initio calculations were performed to obtain the global minima of OH-(H₂O)_n and [OH-(H₂O)_n]⁻ complexes. Geometries of the local minima of the complexes were optimized at the hybrid density functional B3LYP level of theory using a 6-31G (d,p) basis set. The zero-point energy (ZPE)-corrected optimized geometries were calculated using the same method and basis set. No scaling factors were applied. All calculations were carried out using GAUSSIAN 03 (Frisch *et al.*, 2003).

3. RESULTS AND DISCUSSION

3.1 The Optimized Structures and the Energy States of Complexes

Structures of the OH-H₂O, OH-(H₂O)₂, and OH-(H₂O)₃ complexes, optimized at their global minima, are shown in Fig. 1. OH-H₂O and OH-(H₂O)₃ belong to the Cs point group while OH-(H₂O)₂ has no symmetry. The structure of OH-H₂O is consistent with the results of previous studies energy (Karakus and Ozkan, 2005; Aloisio and Francisco, 2000; Wang *et al.*, 1999; Dubey *et al.*, 1997; Xie and Schaefer, 1993; Kim *et al.*, 1991).

A hydrogen bond with a length of 1.875 Å is formed between the hydrogen atom of OH and the oxygen atom of H₂O due to the acceptance of electronic density by OH. The bond lengths and angles of OH and H₂O at their individual global minima were retained in the various complexes.

In OH-(H₂O)₃, two additional H₂O molecules form hydrogen bonds with OH-(H₂O) that are directed 2.5 Å out of the Cs plane. OH-(H₂O)₂ consisting of a six-membered ring formed the hydrogen bonding of the OH radical and two OH groups originating from the H₂O molecules.

The total energies and the Gibbs free energies of the reactants and the complexes at their global minima are listed in Table 1. The binding energy of the OH-H₂O complex ($-6.0 \text{ kcal mol}^{-1}$) is consistent with the results of previous studies (Xie and Schaefer, 1993; Nanayakara *et al.*, 1992). Further hydration via hydrogen bonding before dissociation of the original OH-H₂O complex is expected to stabilize the complex with negative enthalpy changes ($\Delta H_{n-1 \rightarrow n} < 0$).

3.2 Determination of Rate Constants

The transition state in Rxn. (1) was not found at the

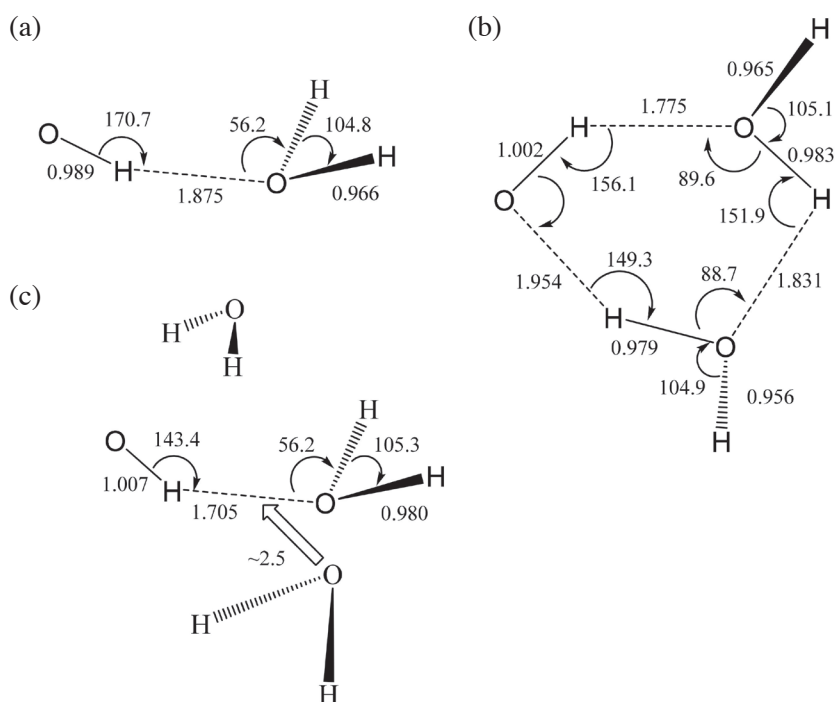


Fig. 1. The structures of (a) OH–H₂O, (b) OH–(H₂O)₂, and (c) OH–(H₂O)₃ were optimized using the B3LYP method and s 6-31G (d,p) basis set. The structures of (a) and (b) belong to the C_s point group.

Table 1. Energies of OH–H₂O and related species (in Hartree).

| Species | Total energy ^a | Gibbs free energy | $\Delta H_{n-1 \rightarrow n}$ ^b (kcal mol ⁻¹) |
|------------------------------------|---------------------------|--------------------------|---|
| OH | -75.720061 | -75.736997 | |
| OH ⁻ | -75.718319 | | |
| H ₂ O | -76.398364 | -76.416020 | |
| OH–H ₂ O | -152.127950 | -152.153581 | -6.0 (-5.7) ^c |
| OH–(H ₂ O) ₂ | -228.546261 | -228.575091 | -12.5 |
| OH–(H ₂ O) ₃ | -304.956232 | -304.989515 | -7.3 |
| OH...H ₂ O ^c | -152.118299 ^e | -152.146902 ^d | |

^aCorrected by zero-point energy

^bEnthalpy change due to water hydration [OH–(H₂O)_{n-1} + H₂O → OH–(H₂O)_n]

^cA loose OH–H₂O complex was substituted for a transition state.

^dOne imaginary frequency was ignored from the energy corrections.

^eNanayakkara *et al.*, 1992

B3LYP and MP2 levels of theory, implying that the entrance barrier is extremely shallow or zero. Therefore, the reaction is assumed to proceed whenever the reactants collide with each other at the proper orientations. The rate constant within a reactive hard-sphere model is calculated by the collision frequency (Z) and the activation energy (E^*) as follows (Steinfeld *et al.*, 1998):

$$k = Z \cdot p \cdot e^{-E^*/k_B T} = \pi d^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} p \cdot e^{-E^*/k_B T}, \quad (6)$$

where d is the hard sphere minimum approach distance (m), k_B is the Boltzmann constant (1.381×10^{-23} J K⁻¹), T is the temperature (298 K), μ is the reduced mass (kg), and p is a steric factor. The distance between two oxygen atoms in the complex (2.86×10^{-10} m) was used as d because the centers of mass are close to the oxygen atoms in both OH and H₂O. Since no entrance barrier ($E^* = 0$) was assumed, the rate constant was calculated as $2.18 \times 10^{-16} \cdot p$ cm³ molecule⁻¹ s⁻¹. The steric factor p was the last variable to be determined.

The steric factor p represents the relative orientation

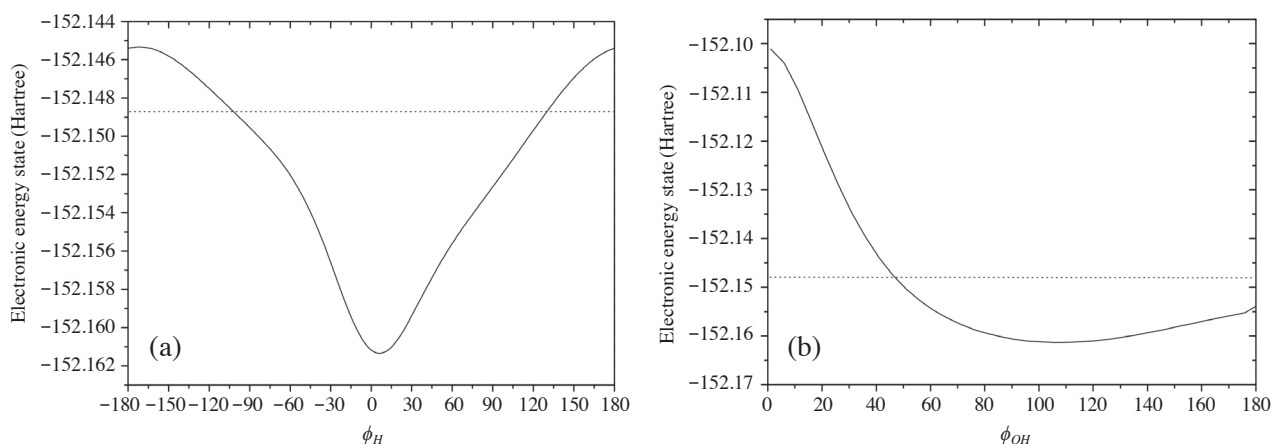


Fig. 2. The energy dependence on molecular orientation. The dotted line is the total energy of the reactants without correcting by zero-point energy. 67% of ϕ_H and 72% of ϕ_{OH} are possible orientations for the complex forming reaction of OH and H₂O.

of the reactant molecules that results in deviations in the reactive hard-sphere model compared to the observed gas-kinetic collision rate (Steinfeld *et al.*, 1998; Laidler and Meiser, 1995; Atkins, 1990; Levine, 1990). Since the quantitative determination of p is beyond the scope of this study, and since no transition state was optimized, an approximate value for p was estimated by scanning the potential energy surface through the variables of ϕ_H , ϕ_{OH} , and d_{O-O} . ϕ_H is the angle of the hydrogen atom in OH relative to the two oxygen atoms in the complex (H–O–O), ϕ_{OH} is the angle of the OH bond relative to the H₂O plane, and d_{O-O} is the distance between the two oxygen atoms assuming a fixed O–H distance in OH. Although the energy dependence on ϕ_H and ϕ_{OH} did not include all possible orientations of the two reactant molecules, a rough estimate of p was possible. The energy dependence on the angles ϕ_H and ϕ_{OH} is shown in Fig. 2(a) and (b), respectively.

According to the data in Fig. 2, most of the possible orientations were favorable for complex formation. When ϕ_H was between -108° and 135° , the energy of the complex was below that of the reactants (-152.1482 Hartree, not corrected by ZPE). Thus, 67% of the possible OH orientations were conducive to the reaction. For ϕ_{OH} , angles greater than 50° , corresponding to 72% of the possible orientations, were appropriate for complex formation. Therefore, p was roughly estimated as 0.48, giving 1.1×10^{-16} cm³ molecule⁻¹ s⁻¹ as the forward rate constant k_f .

In the self-dissociation of the OH–H₂O complex, a loose complex of OH and H₂O (OH...H₂O in Table 1) was assumed as the transition state, although no optimized transition state was found. The structures of OH and H₂O at their individual global minima were retained in the loose complex while the distance between

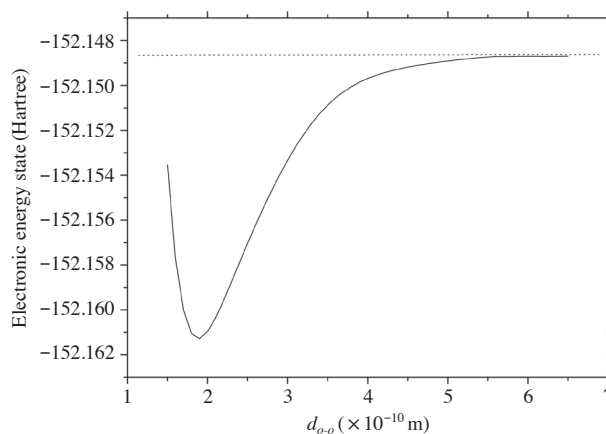


Fig. 3. The energy dependence on d_{O-O} in the loose OH–H₂O complex. The energy of the complex converges at a distance of 5.5 Å, which was used in the calculation for k^{-1}_f .

them was long enough to not interrupt the stability of each species. Fig. 3 shows how the total energy of the complex depends on d_{O-O} and converges at a distance of 5.5 Å. This value was used in subsequent calculations.

The rate constant of the reverse reaction k^{-1}_f was determined using the loose complex (OH...H₂O) and the OH–H₂O complex using the Eyring equation (Laidler and Meiser, 1995; Atkins, 1990):

$$k = \frac{k_B T}{h} e^{\Delta^* S^\ddagger / R} e^{-\Delta^* H^\ddagger / RT} = \frac{k_B T}{h} e^{\Delta^* G^\ddagger / RT}, \quad (7)$$

where h is the Planck constant (6.626×10^{-34} J s), R is the gas constant (8.315 J K⁻¹ mol⁻¹), $\Delta^* S^\ddagger$ is the entropy change between a reactant and a transition state,

Δ^*H^o is the enthalpy change between a reactant and a transition state, and Δ^*G^o is the Gibbs free energy change between a reactant and a transition state.

The Gibbs free energies of the two complexes (Table 1) gave $k^{-1}_1 = 5.3 \times 10^9 \text{ s}^{-1}$ at 298 K. Since this is a first-order reaction, the inverse of the rate constant is the reaction lifetime, $1.9 \times 10^{-10} \text{ s}$. This value implies that the OH–H₂O complex dissociates extremely fast, which is why that clear experimental evidence supporting the existence of this complex has not yet been reported.

Since the self-dissociation of the OH–H₂O complex (reverse of the title reaction) is identical to Rxn. (2) and is extremely fast, the overall rate constant of the H atom transfer reaction [Rxn. (1)-(2)] can be assumed to be k_1 , which agrees with previously reported values (Uchimaru *et al.*, 2003; Dubey *et al.*, 1997).

3.3 Atmospheric and Experimental Implications

The estimated equilibrium constant K_1 , as described in Eq. (8), was $2.1 \times 10^{-26} \text{ cm}^3 \text{ molecule}^{-1}$ using the values of k_1 and k^{-1}_1 determined above.

$$K_1 = \frac{[\text{OH} \cdot \text{H}_2\text{O}]}{[\text{OH}][\text{H}_2\text{O}]} = \frac{k_1}{k^{-1}_1} \quad (8)$$

Since the global average OH concentration ([OH]) in the troposphere during the day and the concentration of H₂O ([H₂O]) at 40% relative humidity are $5 \times 10^6 \text{ molecule cm}^{-3}$ and $3.2 \times 10^{17} \text{ molecule cm}^{-3}$, respectively, the concentration of the OH–H₂O complex ([OH–H₂O]) can be calculated as follows.

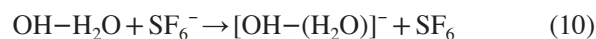
$$\begin{aligned} [\text{OH-H}_2\text{O}] &= K_1 \cdot [\text{OH}] \cdot [\text{H}_2\text{O}] \\ &= 3.4 \times 10^{-2} \text{ molecules cm}^{-3} \end{aligned} \quad (9)$$

Therefore, the fraction of OH–H₂O is relatively small in the troposphere, which means that only $6.7 \times 10^{-7}\%$ of OH radicals are converted into OH–H₂O complexes. Consequently, multiple complexes of OH and H₂O molecules can exist in only negligible amounts. Although the reactivity of the OH–H₂O complex has not been thoroughly studied, possible changes in OH reactivity via Rxn. (1) can be excluded for this reason.

However, one important implication of complex formation between OH and H₂O is evident in experimental studies on atmospheric chemistry. Although several researchers have studied the effects of humidity on OH heterogeneous reactions via chemical ionization mass spectrometry (CIMS) (Park *et al.*, 2013, 2012, 2009, 2008; Molina *et al.*, 2004; Bertram *et al.*, 2001), technical problems arise in experiments conducted under high water vapor pressure conditions. One of these problems is that water vapor significantly reduces the sensitivity of CIMS to OH by the formation of

[OH–H₂O][–] during chemical ionization (Park *et al.*, 2008; Arnold and Viggiano, 2001; Wickramanayake *et al.*, 1995).

The complex ion can originate from two pathways. The first is as the molecular ion of the OH–H₂O complex [Rxn. (1) and (10)]. The second is from the reaction of a cluster of H₂O molecules with a gaseous OH ion (OH[–]), formed in turn by an electron transfer from the ionization agent (SF₆[–]) [Rxn. (11) and (12)].



or,



Although these two pathways are indistinguishable by their mass spectra, the first pathway may be excluded due to the rarity of Rxn. (1). *Ab initio* calculations of the energy of [OH–(H₂O)_n][–] complexes were performed to estimate the reaction behavior of the second pathway. The equilibrium of Rxn. (12) is believed to shift to the left because of the thermodynamically deep energy well of the complex ($-36.5 \text{ kcal mol}^{-1}$). This indicates that the ion product of the OH–H₂O complex observed in CIMS experiments under humid conditions is due to reactions between H₂O clusters and OH[–] ions during chemical ionization, not from the direct ionization of OH–H₂O.

4. SUMMARY

This is the first estimation of the rate constant of the complex forming reaction between OH and H₂O in the gaseous phase based on a reactive hard-sphere model and the Eyring equation. The energy states and the optimized geometries of the reactant, the complex as the reaction product, and the approximate transition state were determined by *ab initio* calculations based on density functional theory. The calculated rate constants of the forward and reverse reactions were $1.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $5.3 \times 10^9 \text{ s}^{-1}$, respectively, and are similar to those obtained in previous studies. The extremely low concentration of OH–H₂O in the troposphere, estimated using the calculated equilibrium constant of the reaction and typical tropospheric conditions, implies that contributions of OH–H₂O formation to changes in OH reactivity can be excluded from atmospheric models. This study additionally showed that the ion product of the OH–H₂O complex, which is often observed in CIMS experiments under humid conditions, results from the reaction of

H₂O clusters and OH⁻ ions that are formed during chemical ionization.

ACKNOWLEDGEMENT

This work was partially supported by NSF and DOE grants.

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(Received 16 March 2015, revised 27 April 2015, accepted 27 April 2015)