Acc. Chem. Res. **2000,** *33,* 825−830

ARTICLES

Radical−Water Complexes in Earth's Atmosphere

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Received May 12, 2000

ABSTRACT
In the atmosphere, many chemical processes are controlled by open-shell radical species. While these species are present in relatively small number densities, they initiate many of the cycles that control the chemistry of the atmosphere. The purpose of this Account is to examine recent studies of radical−water complexes that are composed of atmospherically important species. We hope this Account will provide a report on the status of this topical field, while encouraging new research directions.

I. Introduction

Water is an important component of Earth's atmosphere, playing a major role in its chemistry and radiation absorption, and in atmospheric dynamic processes. It exists in the solid, liquid, and gas phases and readily converts between these phases in the atmosphere. Water is found throughout the atmosphere, although its concentration is highly variable. The amount of water is thought to be primarily controlled by climate processes. The most familiar forms of water in the atmosphere are clouds. Clouds cover approximately 60% of the Earth's surface[1] and can be composed of water in all three phases. Gas-phase water is typically saturated, or even slightly supersaturated, in clouds. Liquid-phase water is also present in clouds as atmospheric aerosols. Solid- and liquid-phase chemical reactions in the aqueous phase are critical to many atmospheric processes.[2] The concentration of water in the gas phase, i.e., water vapor, is heavily dependent on the temperature of the atmosphere. The zonal mean specific humidity is about an order of magnitude higher in the tropical latitudes than it is at the poles.[3] The amount of water vapor also generally decreases with increasing altitude. Water vapor is the most important absorber of infrared light in the Earth's atmosphere. It absorbs most of the infrared light with wavelengths less than 8 μm and greater than 18 μm. Since human activities are thought to have little impact on the water vapor concentration, water is not one of the greenhouse gases included in concern about global climate change for the future.[4,5]

An interesting property of water is its ability to form hydrogen bonds. Hydrogen bonding governs many chemical and biological processes in nature.[6,7] Although hydrogen bonding has been known for quite some time,[8] new research involving hydrogen bonding and hydrogen-bound species continues to produce interesting results. Water possesses the ability to form hydrogen bonds with itself, and hence to form complexes. The prototypical hydrogen-bound system is the water dimer, H_2O-H_2O. The structure of the water dimer has been determined both experimentally and theoretically[9−25] and is shown in Figure 1. The hydrogen bond distance in the water dimer, R, is about 1.95 Å. Thermal conductivity measurements[26] of the enthalpy change for the formation of the water dimer (ΔH) yield a value of -3.6 kcal mol^{-1} at 373 K. While this is widely regarded as the best estimate, the error associated with this number is relatively high, ± 0.5 kcal mol^{-1}. Accurate determination of the well depth, ΔE, has proven to be a difficult task, as zero-point and thermal energy corrections are not easily determined experimentally. Recent calculations[22,25−28] estimate ΔE to be between 4.6 and 5.6 kcal mol^{-1}. Researchers[29−32] have used these data to determine the equilibrium constant for the formation of the water dimer, K_f. The large uncertainty in the binding energy, however, makes accurate determination of this value difficult. At the Earth's surface, these estimates[31,32] yield an equilibrium water dimer mole fraction of 0.1−0.2% under saturated conditions. This means that water dimer number densities can be on the order of 10^{14} molecules cm^{-3}. This would make water dimer as abundant as methane under certain conditions. This is naturally an upper limit, with the mole fraction rapidly decreasing with altitude as the temperature drops, and hence causing a drop in water number density. An exception to this would be in clouds, where saturation of water vapor likely exists. While this is a relatively small fraction of the total amount of water vapor present, recent experiments[33] have shown that water dimer may contribute to new chemical reactions, which are important to the production of sulfuric acid aerosol particles. Furthermore, water dimer and other water complexes have been associated[35] with absorption of infrared light in the water continuum. This is due to two phenomena unique to complexes: shifts in intramolecular vibrational modes due to complexation, and new intermolecular modes unique to the complex. These features of the water dimer have been utilized to detect the species experimentally.[36−44] Fraser[14] has written a review that covers experimental detection of the water dimer done prior to 1991, while Scheiner[25] details theoretical studies of water complexes prior to 1994.

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10.1021/ar000097u CCC: $19.00

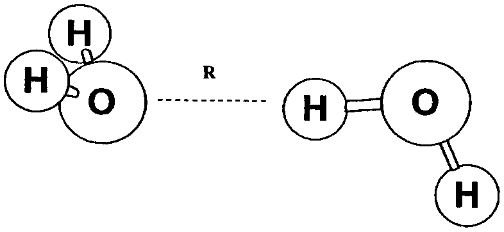

FIGURE 1. Structure of the H_2O-H_2O complex.

The objective of this Account is to review some of the recent discoveries in the field of hydrogen-bound species composed of radicals of atmospheric importance. Recently, water complexes with molecules of ozone[45] and nitric acid[46] have been studied with respect to their atmospheric significance. We will first examine some prototypical complexes, examine the conventional roles these complexes are thought to have in atmospheric chemistry, and finally look at the significance of radical−molecule complexes.

We classify the radical−molecule complexes in this study into two general categories: (a) nonequilibrium and (b) equilibrium. In the former case, the monomers react further to form products, and the reaction follows the general reaction scheme given in eq 1:

$$AB + C \rightarrow AB\cdots C \rightarrow A + BC \qquad (1)$$

AB represents the molecular species, and C represents the radical species. The reactants go through an intermediate complex, AB···C, forming a new molecule A and radical BC. In the latter case, the monomers are unreactive, and an equilibrium is established between the monomers and complex. The general reaction scheme is given in eq 2, where X and Y are the monomers and X···Y is the associated complex.

$$X + Y \rightleftarrows X\cdots Y \qquad (2)$$

The fate of the complex X···Y will be examined for some complexes on the basis of current understanding.

What makes radical−water complexes a special topic to atmospheric chemistry is the fact that radicals are the reactive species which initiate much of the chemistry of the lower atmosphere. Understanding the chemistry of radicals is crucial to being able to describe many atmospheric processes. Reactions between the closed-shell species in the atmosphere are generally slow compared to reactions with radical species. It will be shown that complexation can affect the reactivity of the radical. That is, it can make a reaction go slower or faster. It will also be shown that complexation can affect the photochemistry of the species.

II. Water−Radical Complexes

A. HO_x-H_2O Complexes. Water is known to form complexes with both the hydroxyl (OH) and hydroperoxyl (HO_2) radicals. The hydroxyl radical and water react with each other, essentially exchanging a hydrogen atom and re-forming the reactants.

$$OH + H_2O \rightarrow HO-H_2O \rightarrow H_2O + OH \qquad (3)$$

In this case, the hydroxyl radical−water complex (H_2O-HO) is an intermediate. Hydroperoxyl radical and water react only to form a complex.

$$HO_2 + H_2O \rightleftarrows HO_2-H_2O \qquad (4)$$

In this case, the hydroperoxyl radical−water complex (HO_2-H_2O) is in equilibrium with the reactants, similar to the water dimer. These are prototypical radical−molecule complexes: one as a reaction intermediate, and the other in equilibrium with its parent monomers.

Reaction 3 has been studied using both experimental and theoretical[47−54] methods. Experimental studies rely on isotopic substitution, and an upper limit for the rate constant, k_1, of 2×10^{-16} cm^3 molecule^{-1} s^{-1} has been determined. The reaction proceeds via the formation of an H_2O-HO complex, shown in Figure 2, in which water acts as a hydrogen acceptor and the hydroxyl radical is the hydrogen donor. Xie and Schaefer[48] calculate a minimum structure with a hydrogen bond distance, R, of about 1.94 Å, which is about the same as the water dimer hydrogen bond distance. The well depth (D_e) for this complex is approximately 5.6 kcal mol^{-1}, also similar to that of the water dimer. No experimental studies of this complex have been reported, although it may be possible to detect via high-resolution infrared spectroscopy or matrix isolation spectroscopy.

Hamilton[50] first proposed the complex between the hydroperoxyl radical and water, HO_2-H_2O. Subsequent theoretical calculations[51,52] show that the hydroperoxyl radical acts as the hydrogen donor, and water is the hydrogen acceptor, as shown in Figure 3. Included in the theoretical studies of this complex is work done in our laboratory.[52] We find that the intermolecular bond distance is approximately 1.78 Å, about 8% shorter than in H_2O-HO and H_2O-H_2O. The binding energy (D_o) of the HO_2-H_2O complex is calculated to be about 6.9 kcal mol^{-1}, and a well depth (D_e) of 9.4 kcal mol^{-1} is calculated. Nelander,[53] using matrix isolation infrared spectroscopy, has detected the complex, utilizing the intramolecular shifts in the complex with respect to those modes in the isolated monomer to detect the complex. Five of the six intramolecular modes in that species were detected this way. This and other predicted shifts agree well with what is observed in the matrix isolation experiment. Because HO_2 and H_2O do not react with each other, the HO_2-H_2O complex should be in equilibrium with the monomers. An equilibrium constant (K_c) of about 1×10^{-18} cm^3 molecule^{-1} at 300 K, and 1×10^{-15} cm^3 molecule^{-1} at 200 K, is calculated for the HO_2-H_2O complex. The result is an upper limit for the mole fraction of HO_2-H_2O relative to the total HO_2 concentration of 0.3. This is important to atmospheric chemistry because it shows that the HO_2 self-reaction is faster in the presence of water.[55−57] The rate constant for eq 5, the reaction between the HO_2-H_2O complex and HO_2, is larger than the rate constant for eq 6, the self-reaction of HO_2.

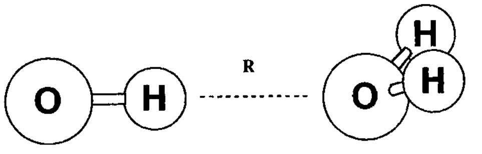

FIGURE 2. Structure of the $OH-H_2O$ complex.

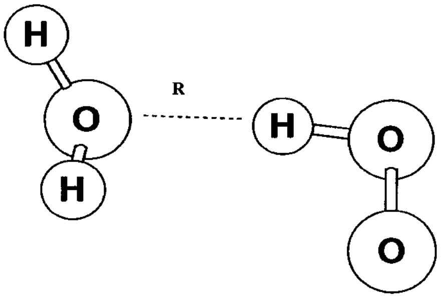

FIGURE 3. Structure of the HO_2-H_2O complex.

$$HO_2-H_2O + HO_2 \rightarrow H_2O_2 + O_2 + H_2O \qquad (5)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (6)$$

This water vapor enhancement[58] is also seen in the reaction between the hydroperoxyl radical and nitrogen dioxide. The authors who studied that reaction speculate that a similar enhancement might be seen in HO_2 reactions with O_3 and ClO.

Radical−molecule complexes can be compared to other types of complexes. In Table 1, we compare the well depths (D_e) of $OH-H_2O$ and HO_2-H_2O with those of molecule−molecule (H_2O-H_2O) and ion−molecule (OH^--H_2O and $H_3O^+-H_2O$) complexes.[59,60] It can be seen that the ion−water complexes are the most strongly bound. The strength of the ion−molecule binding energy stems from a charge−dipole interaction present in these molecules. In terms of binding energy, radical−molecule complexes are more similar to the molecule−molecule complexes, both of which are held together by dipole−dipole interactions. In these cases, the radicals are good hydrogen donors to the water molecule.

B. $HOCO-H_2O$ Complex. The oxidation of carbon monoxide (CO) by the hydroxyl radical (OH), which produces HOCO, an atmospherically important radical species, is an important reaction in the atmosphere and in combustion chemistry, influencing the chemistry of many key cycles.[5] Recent theoretical calculations predict the formation of a $HOCO-H_2O$ complex.[61] While the formation of such a complex in the atmosphere is unlikely due to very low HOCO concentrations, this section is included in this Account because of the role that complexes may have on laboratory experiments performed under conditions where the complex may form. Experiments show[62] that the collisional deactivation of vibrationally excited HOCO is strongly affected by the collision partner, with water being 10 times as efficient a third body as N_2. There is uncertainty as to whether the effective quenching of HOCO* by H_2O affects the results of studies[63] of the mass-independent fractionation (MIF) of oxygen in the reaction of carbon monoxide and hydroxyl radical. There is a conflict in the data concerning the dependence of the rate constant for the OH + CO reaction and the concentration of water. At least one experimental study[64] finds that there is a water concentration dependence on this reaction rate constant. The $HOCO-H_2O$ complex has a six-membered ring structure, which includes all atoms except one hydrogen from water. The calculated intermolecular bond distance is 1.731 Å. The binding energy (D_o) of the complex is 7.1 kcal mol^{-1}, calculated at the same level of theory. The stability of this complex suggests that it cannot be excluded in the analysis of laboratory studies of the OH + CO reaction in the presence of water.

Table 1. Comparison of Different Types of Complexes

complex	type of interaction	well depth, D_e (kcal mol^{-1})	ref
H_2O-H_2O	molecule−molecule	5.0	28
$OH-H_2O$	radical−molecule	5.6	49
HO_2-H_2O	radical−molecule	9.4	53
OH^--H_2O	anion−molecule	27.0	59
$H_3O^+-H_2O$	cation−molecule	33.5	60

C. NO_x-H_2O Complexes. NO_x (NO and NO_2) are important reactive nitrogen species involved in many atmospheric processes.[2,5] NO_x are the most abundant radical species in the atmosphere, with both natural and anthropogenic sources. Water is unreactive toward NO_x, so if a complex between these radicals and H_2O exists, it would be in equilibrium with its parent monomers. A complex between nitric oxide (NO) and water has been observed using matrix isolation experiments and has also been the subject of a theoretical study.[65] Several isomers of the complex that are energetically similar were examined. In the lowest energy isomer of the $NO-H_2O$ complex, H_2O acts as a hydrogen donor, and the nitrogen atom of NO is the hydrogen acceptor. The calculated intermolecular bond distance, R, is approximately 2.66 Å. The author did not report any vibrational frequency calculation values. The $NO-H_2O$ complex is very weakly bound, with a well depth (D_e) of about 1.1 kcal mol^{-1}. Because of the shallow well depth of this complex, it is unlikely that this complex exists under normal atmospheric conditions. There are no published experimental studies of a complex between water and nitrogen dioxide (NO_2). Recently, new studies have shown how the NO_2-H_2O complex may play an important role in the production of nitrous acid (HONO).[66] Nitrate radical (NO_3) is another important NO_x species. We have found no studies of a water complex with NO_3 in the literature.

D. ClO_x-H_2O Complexes. Chlorine oxide radicals play a critical role in stratospheric destruction of ozone. There have been some interesting studies of water complexes with chlorine oxide (ClO) and the isomers of chlorine dioxide (OClO and ClOO). Neither is reactive with water, so we would expect them to behave like the HO_2-H_2O complex in terms of being in equilibrium with their parent monomers. Each case represents interesting new roles complexes may play in atmospheric chemistry.

The formation of the ClO dimer is thought to be a critical step in the depletion of stratospheric ozone over Antarctica.[67,68] The reaction to form the dimer requires the presence of a third body.

$$\mathrm{ClO + ClO + M \rightarrow Cl_2O_2 + M} \qquad (7)$$

Francisco and Sander[69] have suggested that water can act as a catalyst for the self-reaction of ClO, enhancing the rate of formation of the ClO dimer via the following reaction:

$$\mathrm{ClO{-}H_2O + ClO \rightarrow Cl_2O_2 + H_2O} \qquad (8)$$

They calculate a structure for the $ClO-H_2O$ complex in which the water is a hydrogen donor and the oxygen atom of ClO is the hydrogen acceptor. The hydrogen bond distance, R, is calculated to be 2.11 Å. The complex has a calculated well depth (D_e) of 4.4 kcal mol^{-1} and a binding energy (D_o) of 3.2 kcal mol^{-1}. These data suggest that the $ClO-H_2O$ complex should be observable using laboratory experiments. The estimated equilibrium constant for the formation of the complex is between 2.3×10^{-22} and 1.5×10^{-19} cm^3 molecule^{-1}, which is on the order of the equilibrium constant for Cl + CO and Cl + O_2.[70]

Water can form a complex with both isomers of chlorine dioxide. The ClOO isomer is kinetically unstable, dissociating to Cl + O_2, and is involved in the catalytic destruction of ozone.[67,68] Photolysis of OClO proceeds via at least four known channels.[71]

$$\mathrm{OClO} + h\nu \rightarrow \mathrm{ClO + O} \qquad (9)$$
$$\rightarrow \mathrm{ClOO \rightarrow Cl + O_2} \qquad (10)$$
$$\rightarrow \mathrm{Cl + O_2(^1\Delta)} \qquad (11)$$
$$\rightarrow \mathrm{Cl + O_2} \qquad (12)$$

Of these, only the last three result in a net loss of ozone, where $O_2(^1\Delta)$ is excited-state singlet oxygen. The photochemistry of OClO has been shown to be affected by water[72,73] and other polar solvents.[74] The photochemistry of $OClO-H_2O$ has also been studied using matrix isolation spectroscopy.[74] The structures for both $OClO-H_2O$ and $ClOO-H_2O$ have recently been reported.[75] In the $OClO-H_2O$ complex, the water is a hydrogen donor to one of the oxygen atoms of OClO. It has an intermolecular bond distance, R, of 2.56 Å. It has a well depth (D_e) of 3.1 kcal mol^{-1} and a binding energy (D_o) of 2.0 kcal mol^{-1}. In the $ClOO-H_2O$ complex, water is a hydrogen donor to the chlorine atom of ClOO. The intermolecular bond distance, R, is about 2.62 Å. This complex has a slightly smaller well depth, 2.1 kcal mol^{-1}, and binding energy, 1.3 kcal mol^{-1}.

Other halogen oxides play important roles in the chemistry of Earth's atmosphere,[5] particularly BrO and IO. While complexes of water with other halogen oxides are certainly possible, we have found no published data on them. Because the oxygen atoms of these species have an increased electronegativity with respect to ClO, it seems reasonable to expect the complexes of BrO and IO with water to be more strongly bound.

III. Atmospheric Implications

The role radical−water complexes play in atmospheric chemistry is still not well understood. As mentioned, there are two prototypical complexes, one in which the complex is simply in equilibrium with the parent monomers and the other in which the complex is an intermediate and reacts further to give products. The complexes composed of species which do not undergo further reaction present new and interesting roles for these complexes in the chemistry of the atmosphere. Theoretical calculations have shown[53] that equilibrium constants for the formation of these complexes can be quite large. In the case of HO_2-H_2O, up to 30% of the total HO_2 concentration can be in the form of the complex. This leads to the enhancement of the rate constant of the HO_2 self-reaction, due to the faster reactivity of HO_2-H_2O with isolated HO_2. The HO_2-NH_3 complex also produces this effect. Complexation can affect certain reactions, hence changing their atmospheric importance. The pertinent questions that need to be answered include the following: (1) What is the abundance of the complex under atmospheric conditions? (2) What is the effect of complexation on reactivity? To answer these questions, these complexes need to be characterized in the laboratory, in terms of both spectroscopy and reactivity. Complexes of closed-shell species have been implicated in key atmospheric processes. The oxidation of sulfur dioxide, SO_2, to sulfuric acid, H_2SO_4, is an important atmospheric process leading to inorganic aerosol production.[2] In that reaction sequence, sulfur trioxide, SO_3, reacts with water to produce H_2SO_4. Experiments show[33,78−80] that the rate of conversion of SO_3 to H_2SO_4 is second order with respect to water concentration. This led researchers to believe that the reaction of this complex with another H_2O may be an important path leading to H_2SO_4. An alternative explanation is that SO_3 reacts with the water dimer to form H_2SO_4. To date, the mechanism for this reaction remains a matter of debate. This example of the differing reactivity of closed-shell species due to complexation illustrates how important the study of much more reactive open-shell complexes can be. Identification of these complexes in the laboratory and in the atmosphere will provide critical information on their roles in atmospheric chemistry. Complexes also provide the bridge between free isolated molecules and aerosols, whose known role in atmospheric chemistry is becoming more and more apparent. The process of going from free molecule to complex to aerosol is not fully understood. This is an area of research that deserves increased attention. Finally, researchers have shown that water−ozone[46] and water−nitrous oxide[76] complexes have different photochemistry than their isolated parent monomers. This is also seen in the case of the $H_2O-OClO$ complex.[72,73] Overall effects of the photochemistry of complexes also need to be examined. Studies[77] on the excited states of the HO_2-H_2O complex suggest that the photochemistry of HO_2 is affected by complexation. While the excited bands of HO_2 are inaccessible in the lower atmosphere, shifts in the HO_2 spectra by complexation allow photochemical channels to be accessed at longer wavelengths and, as a result, switches on the HO_2 photochemistry in the lower region of the atmosphere. Shifts in the excited-state spectra as a result of water complexation may affect the photochemistry of the atmosphere.

Complexes not involving water also need to be explored, especially those involving good hydrogen donors and acceptors, as they are likely to form more stable complexes. The reactive intermediate of the hydroxyl radical (OH) and nitric acid (HNO_3) is one example of this type of complex that has been studied.[81,82] One illustration of non-hydrated complexes that may be particularly significant is the understanding of how radicals produced in the lower region of the atmosphere could form complexes with the vast array of organic species prevalent in the troposphere. These studies should also provide important fundamental knowledge necessary to understanding how organic aerosols are formed. It is clear that there are many interesting avenues of work in this area of atmospheric chemistry that can be performed, and it is also clear that new fundamental knowledge of hydrogen-bound systems can be derived from these studies.

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