

Heterogeneous Reactions Important in Atmospheric Ozone Depletion: A Theoretical Perspective

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ABSTRACT

Theoretical studies of the mechanisms of several heterogeneous reactions involving ClONO₂, H₂O, HCl, HBr, and H₂SO₄ important in atmospheric ozone depletion are described, focused primarily on reactions on aqueous aerosol surfaces. Among the insights obtained is the active chemical participation of the surface water molecules in several of these reactions. The general methodology adopted allows reduction of these complex chemical problems to meaningful model systems amenable to quantum chemical calculations.

1. Introduction

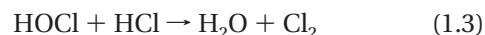
It is not always appreciated that the discovery of the ozone hole in the Antarctic stratosphere in 1985¹ came as a shock to the Atmospheric Chemistry community and required a dramatic change in thinking about how the chemistry responsible might actually occur. As is well-known, Molina and Rowland² proposed that the photolysis by ultraviolet radiation of chlorofluorocarbons, which rise to the stratosphere, produces chlorine (Cl) radicals and that these transform ozone (O₃) into oxygen (O₂) in a catalytic cycle. However, it was subsequently realized that these Cl radicals end up, via gas-phase reactions, as the “reservoir species” hydrochloric acid (HCl) and chlorine nitrate (ClONO₂), essentially nonreactive with respect to gas-phase chemistry. The 1985 ozone hole magnitude far exceeded that expected via gas-phase reactions. That heterogeneous chemistry provided the resolution of this

dilemma was proposed in 1986 by Solomon et al.³ Briefly, in the Antarctic winter, polar stratospheric clouds form at ~190 K, containing several types of aerosol particles, some of which are ice particles. On these aerosols, the net heterogeneous reaction



generates nitric acid (HNO₃) and, most importantly, molecular chlorine (Cl₂), which with the sun's return in the Antarctic spring is photolyzed to produce Cl radicals, which then activate the ozone depletion cycle.⁴

Reaction 1.1 on an ice surface was an unfamiliar one when it was proposed, and a number of important experimental laboratory studies of it and related reactions were undertaken.⁵ Despite the considerable progress made via those studies, a number of issues remained unresolved. Does the mechanism occur in one step, as written, or in the two steps



involving the initial hydrolysis of ClONO₂ to produce hypochlorous acid (HOCl) with subsequent reaction with HCl to produce Cl₂? What is the role of the ice? Does it merely serve as a “platform on which the reactants meet or as a source of solvation, or does it have some other function?

Here, we highlight theoretical work aimed at answering these and other questions. Theory's role here is important; it can address issues at the molecular level not easily examined via experiment. Our primary focus is on the above heterogeneous reactions in the Antarctic stratosphere, but we also discuss related reactions of importance in significant ozone depletion elsewhere, that is, in the Arctic troposphere and in the mid-latitude stratosphere. Space limitations oblige us to refer the reader to our original papers for literature support for unreferenced statements herein, as well as for more complete discussions and references.

2. Chlorine Nitrate Hydrolysis

When we began our theoretical work on the net reaction 1.1, there was a certain predominance of thought that the two-step mechanism (reactions 1.2/1.3) was the operative one, and the ClONO₂ hydrolysis (reaction 1.2) was investigated first.⁶ Available experiments indicated that the hydrolysis was “rapid”⁵ and that the Cl–ONO₂ bond—in which the Cl is electropositive—is broken.⁷

An interesting mechanism had been proposed⁸ involving the nucleophilic attack of a H₂O on Cl to produce the [H₂OCl]⁺ ion coordinated to the nitrate ion (NO₃[−]).

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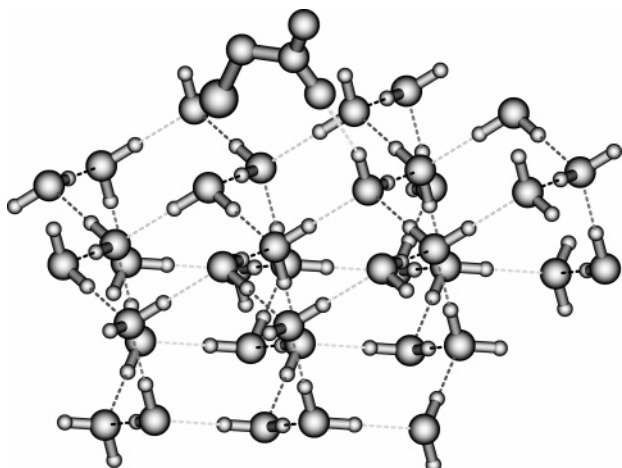


FIGURE 1. Model of ClONO₂ adsorbed on ice.

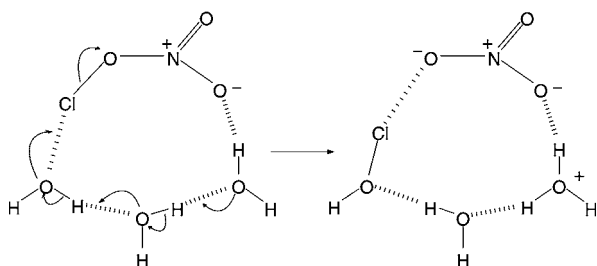


FIGURE 2. ClONO₂ hydrolysis mechanistic hypothesis.

However, water's relative weakness as a nucleophile seemed inconsistent with the rapidity of the hydrolysis.⁶ Further, [H₂OCl]⁺'s existence had been ruled out in extensive aqueous solution phase experiments in the 1960s,⁹ a point reiterated^{10,11} specifically for the ClONO₂ hydrolysis.

An alternate mechanism was suggested⁶ by modeling the possible arrangement of a ClONO₂ on an ice surface (Figure 1) and guided by the need to have a potent nucleophile to effect a rapid hydrolysis. In our mechanistic hypothesis, a proton relay through a water chain in the ice (Figure 2) would generate both a hydroxide (OH⁻) ion-like moiety next to the Cl, providing the required nucleophilic strength to easily break the Cl–ONO₂ bond, and a hydronium ion (H₃O⁺) next to the NO₃⁻ being produced in the nucleophilic substitution (S_N2), thus indirectly weakening the Cl–ONO₂ bond.

We pause to describe our general computational procedure for such reactions.^{6,12–16} The first step consists of assembling a core reaction system (CRS) comprising the key reaction participants and a few waters possibly engaged in proton transfer (PT), as indicated by the mechanistic hypothesis. The next step involves addition of further waters to provide solvation to selected moieties in the CRS. This differentiation, for a model reaction system whose size is computationally demanding, allows limitation of the quantum description to a meaningful CRS, while treating classically those waters with a purely solvating role. Another crucial feature of this procedure is the structural stabilization of the CRS along the reaction path, which results from the natural constraints imposed by the network of solvating waters; a quantum-mechanical

(QM) calculation including only a small CRS would result in its likely collapse and in artificial structures no longer representative of the real system. Transition state (TS) location constitutes the calculation's bottleneck, due to the involvement of the hydrogen bonds in the water network, weakly influenced by changes in the CRS charge distribution, and the interplay between the H₂O⋯ClONO₂ S_N2 and its coupled PT. However, the exploration of the potential energy surface with constrained S_N2 and PT coordinates is a slow albeit safe procedure to reach the TS region. Reactant and product complexes are finally located via calculation of the intrinsic reaction coordinate path starting at the TS (Figure 3).

Returning now to the ClONO₂ hydrolysis, electronic structure calculations of the TS and the reaction path for ClONO₂ forming a ring with three waters and with three extra waters H-bonded to the ring waters to provide solvation for the various ionic species produced along the path confirmed the coupled S_N2/PT mechanism in Figure 2 with an estimated barrier height of 3 kcal/mol⁶ in good accord with experiment.

The mechanism in Figure 2, supported in subsequent theoretical studies,^{17–19} has two important features. It indicates that the water network plays an active role in the reaction beyond the previously expected roles of providing a site for the reactants to find each other and providing solvation for any ionic species involved. This aspect is crucial, since the estimated barrier for the coupled S_N2/PT mechanism involving the first PT in Figure 2 is predicted to rise to at least 30 kcal/mol in the absence of this PT.¹⁰ Further, this mechanism explains the experimental finding that the ClONO₂ hydrolysis, while initially fast on a neat ice surface, slows considerably as the surface becomes acidic:²⁰ the critical PT from the attacking water to the lattice is suppressed by the surface acidification by the HNO₃ produced in the hydrolysis.⁶

3. HCl + ClONO₂ → HNO₃ + Cl₂ on Ice

In view of the results just described concerning the “poisoning” of the ClONO₂ hydrolysis route to Cl₂ production, attention was turned to the mechanism and barrier height for the direct reaction 1.1.¹²

An initial (and historically the first) question to be posed is whether HCl in eq 1.1 is molecular or dissociated into Cl⁻ and H₃O⁺. Here we discuss this acid ionization in the context of reaction 1.1, reserving for section 4.1 the issue of acid ionization in the ClONO₂'s absence. The mechanistic hypothesis for the HCl + ClONO₂ reaction (Figure 4) has strong similarity to that of the ClONO₂ hydrolysis and informed the choice of the model system for reaction 1.1. This involves a CRS comprising HCl, ClONO₂, and two H₂O's, structurally stabilized and solvated by seven extra H₂O's (Figure 5). Electronic structure calculations at the MP2//HF level for the reaction path for the HCl·ClONO₂·(H₂O)₉ model system for reaction 1.1 produced the mechanism whose reactant complex (RC) and TS are displayed in Figure 5. In this study, a useful simplification was offered by the methodology²¹ for cal-

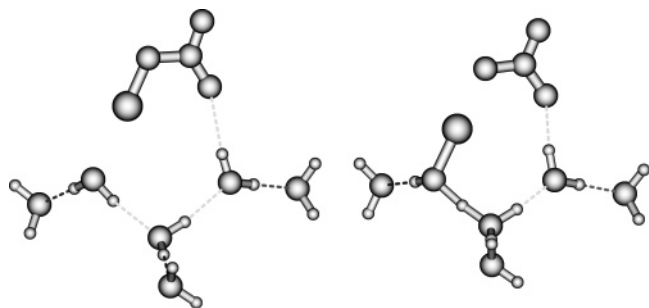


FIGURE 3. ClONO₂ hydrolysis RC (left) and TS (right).

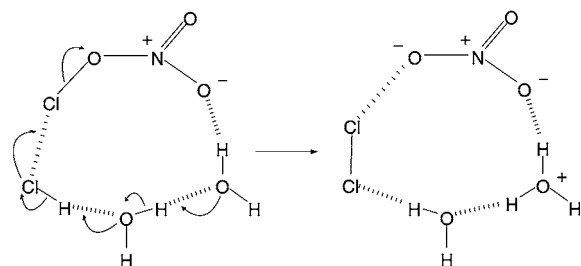


FIGURE 4. HCl + ClONO₂ reaction mechanistic hypothesis.

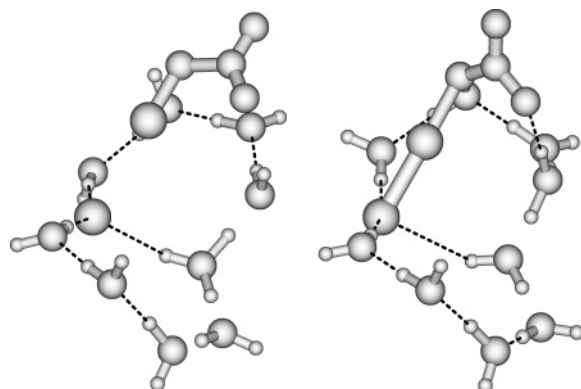


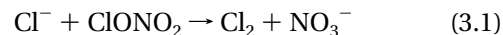
FIGURE 5. HCl + ClONO₂ reaction RC (left) and TS (right). Both Cl's and the O of the water H-bonded to the attacking Cl lie in the page's plane.

ulation of the structures along reaction paths—an expensive aspect of the whole procedure—at low level of theory, that is, HF/3-21G*, followed by the retracing of the low-level reaction path with single-point MP2/6-31+G* energy calculations at selected structures.

First, it was found that in the RC the HCl was spontaneously ionized to produce a contact ion pair (Figure 5). The presence of H₃O⁺ next to Cl⁻, however, impedes the nucleophilic attack on the electropositive Cl of ClONO₂ by engaging the Cl⁻ electrons. Thus, the reaction has to proceed by a PT from this H₃O⁺ to the neighboring water in the chain, freeing the electrons of the Cl⁻ ion for the nucleophilic attack. This PT also assists the reaction by stabilizing the incipient NO₃⁻ produced. Figure 5 shows the calculated TS, in which both the S_N2 features in the Cl^{δ-}⋯Cl^{δ+}⋯ONO₂^{δ-} subsystem and the PT from the H₃O⁺ to the water next to the nitrate group are evident. Detailed study of the reaction path characteristics showed the PT slightly in advance of the S_N2. However, these are simultaneously in train at the TS, a situation we termed a “coupled S_N2–PT process”.

The barrier height was estimated to be 6.4 kcal/mol,¹² sufficiently low to establish the theoretical viability of the direct reaction 1.1 on ice. Again, as for the ClONO₂ hydrolysis, PT within the water network is involved, and thus the latter is an essential chemical partner in this mechanism also. This PT-assisted mechanism has been supported in a subsequent study.²² A technically important aspect in ref 12 was the finding of strong similarity in both the structure and energetics of the MP2//HF and HF reaction paths, thus allowing computationally less intensive HF calculations for this class of model systems.

There is a variant of reaction 1.1 to consider in which the proton is absent, that is, the reaction on ice



which could occur if the proton is transported away from the reaction site or if acid ionization of HCl occurs at another site, and the proton is transported away before the chloride ion's encounter with ClONO₂. The gas-phase version of reaction 3.1 is quite exothermic and is essentially barrierless.²³ However, while some condensed phase reaction thermodynamics were estimated via a dielectric continuum solvation model,²³ no reaction barrier on ice estimate was provided. That there could be such a barrier is already clear from the fact that reaction 3.1 is S_N2. It is well-known from aqueous solution work²⁴ that a barrier can arise in such an environment. The TS for reaction 3.1 should involve delocalization of charge over the [Cl⋯Cl⋯ONO₂]⁻ moiety, in contrast to the charge-localized character of the RC (i.e., Cl⁻⋯ClONO₂); the differential solvation will thus favor the RC compared to the TS.

The estimation of the reaction 3.1 barrier on ice was thus undertaken¹⁴ for a Cl⁻·ClONO₂·(H₂O)₈·W₂₉ model reaction system at the HF level, using effective core potentials for the heavy atoms in the Cl⁻·ClONO₂·(H₂O)₈ QM portion of the model reaction system and an embedding network of classical, polarizable waters (W's). The calculated reaction path (and TS) character was just that anticipated in the discussion introducing this section: the path displays a progressive desolvation of the attacking Cl⁻ and a progressive solvation of the incipient NO₃⁻. Solvation thus leads to a considerable change from the gas-phase reaction: for 0 K, the calculated exothermicity and barrier height are -10.7 and 5.7 kcal/mol, respectively. Significantly, the latter is quite close to the 6.4 kcal/mol barrier height for reaction 1.1, the version with the proton participating in the reaction.

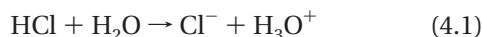
Thus, within calculational uncertainties, reactions 1.1 and 3.1 are equally viable, the choice between them then becoming the issue of whether the proton produced in the HCl acid dissociation at the ice surface is or is not transported from the reaction site. A major point is that the direct reaction between HCl or Cl⁻ and ClONO₂ is evidently the preferred reaction route on acidified surfaces;^{20,25} as noted in section 2, the alternate indirect two-step route would be “shut down” by the poisoning of the ClONO₂ hydrolysis under acidic conditions. In such acidic

conditions, it seems more likely that the proton is present such that the reaction 1.1 is favored, but this remains to be proven.

4. Heterogeneous Acid Ionization in the Atmosphere

While the Antarctic stratosphere ozone hole is most well-known, there is in fact significant ozone depletion in various atmospheric regions, and acid ionization is important in each of them. We discuss, in turn, HCl, hydrobromic acid (HBr), and sulfuric acid (H₂SO₄).

4.1. HCl. We have already discussed in section 1 the HCl dissociation



at an ice surface in connection with reaction 1.1 with ClONO₂, and we return to this issue, but now in the absence of the reactant ClONO₂.

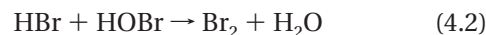
Early experiments²⁰ indicated that HCl uptake from the gas phase by an ice surface was limited in extent to approximately a monolayer. Further, comparison with the much weaker hydrofluoric acid (HF) (much smaller uptake) and the stronger HBr (greater uptake), suggested that the acid dissociation (eq 4.1) was very likely involved.²⁶ It was also suggested²⁷ that a “liquid-like layer” existed at the ice surface under Antarctic stratospheric conditions; if this were so, HCl would naturally be expected to dissociate, since it is a strong acid in liquid water.

The HCl acid dissociation on ice was studied in Boulder^{10,28,29} via molecular dynamics (MD) simulations exploiting methodologies employed for the corresponding reaction in liquid water.³⁰ It was argued that HCl would not ionize atop the ice surface (with the acidic proton coordinated to a lattice water molecule, but no H-bonds to Cl), due to a lack of sufficient solvation of the Cl required to stabilize the incipient Cl⁻. (The assumption of no acid ionization for the HCl atop the surface was supported in a different type of calculation not involving MD.¹⁰) An incorporation mechanism of HCl similar to that of a H₂O under dynamic surface conditions³¹ was proposed.²⁸ A HCl molecule so incorporated in the ice surface region has considerable solvation of both its H and Cl ends. With a HCl placed in assorted locations consistent with such incorporation, calculations^{28,29} indicated that the PT reaction 4.1 was thermodynamically favored with a small activation barrier (~2 kcal/mol). No “liquid-like layer” was found²⁹ or required for the dissociation. Most subsequent theoretical work, involving combined Monte Carlo/ab initio calculations on small HCl/water clusters,³² QM/MM^{33,34} or Car–Parrinello methods,³⁵ without any proton quantization, has focused on the feature that HCl can obtain sufficient solvation of its Cl end and thus dissociate atop the surface in arrangements where two HOH...ClH H-bonds exist involving surface dangling OH bonds (a situation not accounted for in ref 10). However, whether such arrangements are common under polar stratospheric conditions is not known. When only one dangling OH bond solvates the Cl, the HCl adsorbs

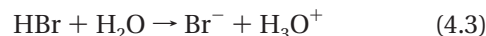
molecularly on the surface and does not ionize,^{34,35} as anticipated.^{28,29} MD simulations of such a molecular HCl indicate that it can readily be incorporated into the ice surface region,³⁶ where it should promptly dissociate.^{28,29}

Thus, several possible mechanisms for HCl dissociation on ice are now available; which of these is (are) actually relevant definitely needs sorting out in future work.

4.2. HBr. In the springtime Arctic tropospheric boundary layer, where bromine is much more abundant than elsewhere, heterogeneous bromine chemistry is implicated in extremely rapid ozone depletion near ground level, and HBr is among the “reservoir species” involved.^{37,38} Heterogeneous reactions such as



“activate” the HBr by producing the readily photolyzable Br₂, effective in gas-phase catalytic ozone destruction cycles.³⁷ Among the relevant surfaces for such reactions is ice. Reactions such as eq 4.2 make the issue of the HBr acid dissociation on ice



under Arctic boundary layer conditions (230–250 K) of interest. Experiments^{5,26,39} indicate that the uptake of HBr by ice exceeds that of HCl and that this is probably related to the acid’s dissociation.

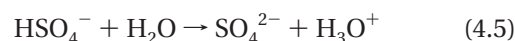
The theoretical study of reaction 4.3¹³ involved two calculations on model ice surfaces. In the first, the possibility that HBr might ionize atop the ice surface was examined via HBr positioning atop a model (H₂O)₁₃ ice lattice. The calculations were performed at the MP2 level, using effective core potentials for the heavy atoms. HBr was positioned initially with its hydrogen H-bonded to an accepting surface water, and it was found that HBr does not ionize atop a “dry” ice surface. In the second case, an additional extra-lattice H₂O, H-bonded to the Br of HBr, was added, motivated by the considerations described in this section’s HCl portion concerning the ice surface dynamic character, which should be even more important at the Arctic boundary layer higher temperatures. The specific question addressed was whether, due to its greater acid strength compared to HCl, HBr could dissociate in such a surface environment in which it finds itself in a ring of waters, even without the benefit of incorporation into the ice lattice. The result¹³ was that HBr acid ionization readily occurs. In a comparison calculation for HCl with one extra-lattice H₂O, such ionization did not occur,⁴⁰ reflecting the importance of HBr’s greater acid strength compared to HCl in overcoming the reduced solvation conditions for the incipient Br⁻.

There is as yet no theoretical study of HBr reactions with other reservoir species, such as eq 4.2. Many of the issues that arose for the HCl + ClONO₂ reaction (section 3) will likely occur here as well. For example, a possible mechanism for reaction 4.2 is much as in Figure 4, in which the Br⁻ nucleophilic attack on the electrophilic Br of HOBr is assisted by a proton relay from a H₃O⁺ through a water chain to eventually protonate the produced OH⁻

like moiety to form the water product. Alternatively, if the proton from the HBr dissociation is transported far from the reaction site, a simple S_N2 reaction of Br^- with HOBr can be envisaged.

4.3. H_2SO_4 . In the mid-latitude stratosphere, away from the poles, the aerosols providing heterogeneous reaction sites are sulfate aerosols (SA), highly concentrated, supercooled (210–240 K) aqueous solutions of H_2SO_4 , with a H_2SO_4/H_2O molecular ratio of ~ 0.1 – 0.4 .⁴¹ Important reactions connected with ozone depletion here include the hydrolyses of dinitrogen pentoxide (N_2O_5)^{42,43} and bromine nitrate ($BrONO_2$).⁴⁴ SA are also found in the Arctic boundary layer, where assorted heterogeneous reactions on/in them are implicated in ozone depletion.^{37,45}

There are two dissociations to be considered for diprotic H_2SO_4 , to produce bisulfate (HSO_4^-) and sulfate (SO_4^{2-}) ions:



The bulk SA ionic composition is well described by thermodynamics models,⁴⁶ so that at a given temperature and relative humidity, the $H_2SO_4/HSO_4^-/SO_4^{2-}/H_3O^+/H_2O$ ratios can be regarded as known for a given H_2SO_4 weight percentage. However, the surface composition is unknown; for example, surface infrared spectroscopic studies admit different interpretations.^{47,48} A key question is whether the surface and bulk compositions differ. One can conceive, for example, that for a bulk composition consisting exclusively of $HSO_4^-/H_3O^+/H_2O$, molecular H_2SO_4 could be produced in the surface region, due to reduced solvation conditions, via PT from H_3O^+ to HSO_4^- .

The very first steps in addressing this issue have involved studies^{15,16} of the first acid ionization (reaction 4.4) on a model aqueous surface. In the first of these,¹⁵ a $H_2SO_4 \cdot (H_2O)_6 \cdot W_{27}$ system was examined in which an initial H_2SO_4 configuration was selected that could produce H_3O^+ readily available for heterogeneous reactions but that involved reduced solvation conditions. If acid ionization occurred readily here, it would also occur in other configurations providing greater solvation. The H_2SO_4 moiety was positioned with each of its OH groups located in the top surface layer, each H-bonded to a H_2O .

The first acid dissociation of H_2SO_4 in this study was not thermodynamically favorable with a 0 K endothermicity of 3.5 kcal/mol.¹⁵ This result is surprising given previous theoretical work indicating that this dissociation proceeds spontaneously in very small water clusters, for example, $H_2SO_4 \cdot (H_2O)_4$.⁴⁹ This raises an important general issue. In fact, HCl and HBr have also been calculated to acid ionize in small water clusters,^{50,51} even though their (and H_2SO_4 's) behavior at model aqueous surfaces described above differs considerably, and even though, for example, the estimated aqueous phase first acid dissociation constant for H_2SO_4 is some 4–5 orders of magnitude smaller than that for HCl. As has been pointed out,¹³ there

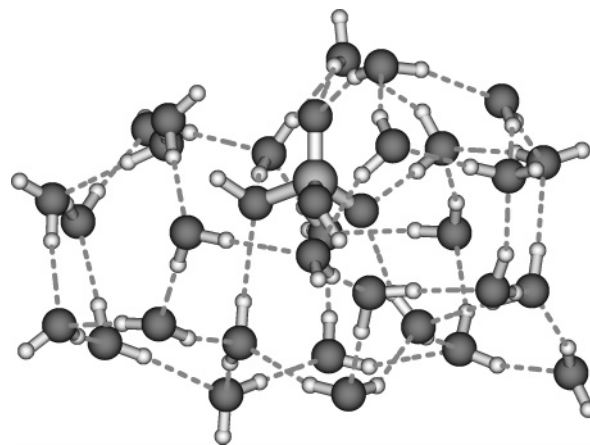


FIGURE 6. $H_2SO_4 \cdot (H_2O)_4 \cdot W_{26}$ model system TS structure.

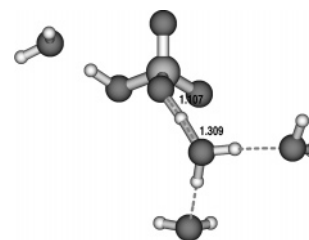


FIGURE 7. $H_2SO_4 \cdot (H_2O)_4$ CRS TS structure. Orientation as in Figure 6.

are important constraints imposed by an extended water network preventing the sort of structural rearrangements that promote dissociation in very small clusters.

The first H_2SO_4 study¹⁵ has been extended¹⁶ by investigating the ionization of the surface region H_2SO_4 proton H-bonded to a bulk H_2O for a model reaction system comprising a $H_2SO_4 \cdot (H_2O)_4$ CRS described at the HF level embedded in a cluster of classical polarizable waters¹⁶ (Figure 6). In this arrangement, acid dissociation is more likely (though not guaranteed) in view of the bulklike character of the proton's location and the extensive H-bonding to the sulfate oxygens. Referring to Figure 7, the water coordinated to the potentially dissociating proton has, in turn, its two protons H-bonded to two other quantum waters, in anticipation of H_3O^+ formation, whereas the water H-bonded to the other, nondissociating H_2SO_4 proton, is simply coordinated to classical waters. Results corrected for zero-point energies and electron correlation¹⁶ indicate that H_2SO_4 dissociation is facilitated by a higher degree of solvation of the sulfate group and lower temperatures. However, even for the cases with better sulfate group solvation, ΔG is positive (~ 0.2 – 1.5 kcal/mol) in the 210–240 K temperature range relevant for SA and at higher temperatures.

Thus, the first H_2SO_4 acid dissociation need not occur at SA surfaces. Of course, the above model systems are far from the highly concentrated SA conditions; an alternate approach to the ionization issue is indicated below.

5. Concluding Remarks

As described within, theory has begun to provide significant insights for a variety of heterogeneous reactions crucial for atmospheric ozone depletion. Among the important lessons learned is that the water molecules at an aerosol surface can play an active chemical role in catalyzing these reactions via proton relay mechanisms and that small cluster calculations are not necessarily representative of surface environments. Despite this encouraging progress, much remains to be done. We forego a litany of the extensive opportunities and challenges for theory here, and simply mention a few outstanding issues.

As noted in section 4.3, SA have a pervasive importance in various atmospheric regions. Beyond their incidence and reactions on them mentioned there, it has been suggested⁴ that SA, rather than ice, might in fact provide the most important reaction sites for the key Antarctic stratosphere reaction between HCl and ClONO₂ (section 3). The issue of the surface ionic composition of these highly acidic aerosols outlined in section 4.3 is a particular challenge, not least due to the elevated H₂SO₄ concentrations and the several PT reactions involved. This issue is pressing, since it is quite likely that the surface region molecules and ions will participate chemically in the assorted atmospherically relevant heterogeneous reactions. Our own efforts here⁵² involve the generalization of a reactive Monte Carlo method⁵³ to deal with the numerous PT reactions in play.

Yet another type of aqueous aerosol surface needs theoretical attention. Aerosols involving nitric acid (HNO₃) are important in upper troposphere (UT) chemistry,³⁹ as well as for stratospheric chemistry.⁴ In the UT, cirrus clouds (covering up to 30% of the Earth's surface) can involve considerable uptake of HNO₃ on water ice, important, for example, in connection with heterogeneous reactions, such as those in sections 1 and 2, on the resulting particles, leading to catalytic ozone destruction. Although HNO₃ acid ionization is plausibly implicated,⁵⁴ a microscopic picture of the HNO₃ uptake is currently lacking, and various reactions on the surface await theoretical examination.

Heterogeneous reactions on other aqueous aerosols are key in generating Cl₂ and Br₂ gases. In the marine boundary layer, aqueous sea-salt aerosols contain high surface concentrations of halide ions, for example, Cl⁻, an initially unexpected situation predicted theoretically.⁵⁵ The Cl⁻ ions can then react with incident OH radicals to produce chlorine radicals, which subsequently combine to form Cl₂.⁵⁵ Such radical-ion reactions will no doubt receive future attention.

Finally, theory has an important role to play in developing methodologies necessary to interpret experimental probes promising incisive insights on atmospherically relevant surfaces. One example here is developments^{56,57} for surface-sensitive infrared sum frequency generation spectroscopy;^{47,48} generalization of these developments to a dynamic situation could provide new insights on the mechanisms of the heterogeneous reactions themselves.

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