

Hydroxyl Radical at the Air–Water Interface

Martina Roeselová,^{*,†,§} John Vieceli,[†] Liem X. Dang,[‡] Bruce C. Garrett,[‡] and Douglas J. Tobias^{*,†}

Department of Chemistry, University of California, Irvine, California 92697, and Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352

Received July 23, 2004; E-mail: martina.roeselova@uochb.cas.cz; dtobias@uci.edu

The interaction of the hydroxyl radical with water is of great interest because of the role of OH radical as a major oxidant in many biological, environmental, and man-made aqueous media. The uptake of hydroxyl radicals on aqueous surfaces is particularly important for atmospheric chemistry, as many atmospherically relevant reactions occur in or on aqueous atmospheric aerosols, cloud droplets, and thin water films on solid surfaces.¹ Understanding the uptake process as well as knowing whether the OH radical has larger propensity for surface or bulk solvation is essential for atmospheric modeling and for elucidating the mechanisms of heterogeneous reactions taking place in the atmosphere. A recent molecular dynamics study of OH impinging on aqueous surfaces² as well as ab initio studies of the microsolvation of OH in small water clusters^{3,4} indicated that, similarly to the hydroperoxy radical (HO₂),⁵ the hydroxyl radical might preferentially bind to the water surface. In the present communication, we report the results of molecular dynamics computer simulations that provide molecular level insight into the process by which a gas-phase hydroxyl radical with thermal impact velocity becomes accommodated at the water surface and/or taken up into the bulk liquid. In addition, the thermal and mass accommodation coefficients of OH on liquid water are reported, and partitioning of OH radicals between the interface and bulk under tropospheric conditions is predicted.

A water slab with two vacuum–liquid interfaces was employed as a model of an aqueous droplet, using 864 water molecules in a 30(*x*) × 30(*y*) × 100(*z*) Å simulation box. The *z* dimension is perpendicular to the water surface. This simulation cell has been previously shown to provide a reasonable model for a small patch of the air–water interface.⁶ Both OH and water were modeled using empirical potentials that explicitly include induced polarization.^{7,8}

To examine the propensity of the OH for the air–water interface, five OH radicals were placed inside the bulk liquid region of the water box equilibrated at *T* = 300 K, and the system was propagated for 3 ns. During this time, the OH radicals were observed to diffuse through the interior of the water slab; however, they were predominantly located in either of the two interfacial regions. Desorption of OH from the surface was also observed a number of times. The density profile of the OH radical is shown in Figure 1, together with a typical snapshot from this simulation.

To study the uptake of OH on a water surface, initial conditions were prepared by placing a single OH radical about 15 Å above the interface at different grid points in the *xy* plane. Initial OH velocities were sampled from the Maxwell–Boltzmann distribution at 300 K subject to the constraint that the *z* component of the center of mass velocity is directed toward the surface. A total of 250 trajectories were run for 90 ps. The results are summarized in Figure

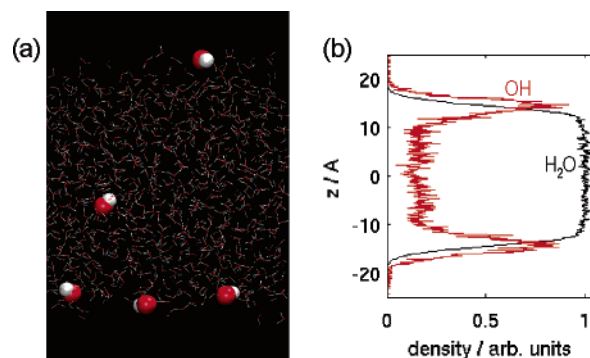


Figure 1. (a) A snapshot from the simulation of five OH radicals in the water slab. (b) Density profiles of OH (in red) and H₂O (in black) indicating the propensity of OH for the air–water interface.

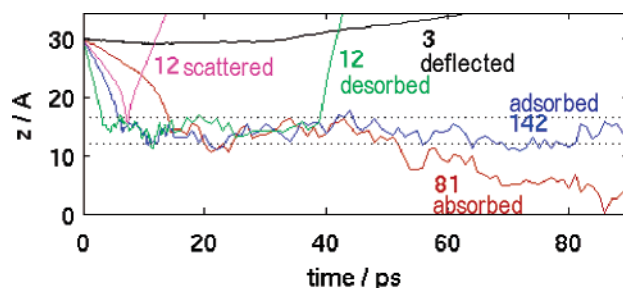


Figure 2. Summary of results of 250 scattering simulations showing the various different outcomes of the OH collision with the water surface. The interfacial region is indicated by the dotted lines, and *z* = 0 corresponds to the middle of the water slab.

2. On the basis of the above data and the fact that the OH radicals reach thermal equilibrium with the liquid water within 4 ps of striking the surface, the thermal accommodation coefficient, *S*, defined as the fraction of collisions with the surface that result in thermal accommodation of OH at the interface, is determined to be *S* = 0.95 at 300 K.⁸ The mass accommodation coefficient, *α*, defined as the probability that OH radicals thermally accommodated at the interface will be incorporated in the bulk liquid rather than desorb, is found to be *α* = 0.83 at 300 K.⁸ This value is much larger than the experimental value of ~0.004.^{9,10} However, it agrees with previous MD studies on other hydrogen-bonding systems^{11–13} that predict *α* close to unity for thermal collisions, often in contradiction with the experimental values. This discrepancy is still under investigation.¹⁴

To assess the equilibrium solvation behavior of OH, a free energy profile for transfer of an OH radical across the air–water interface was calculated using a constrained molecular dynamics technique.¹⁵ The radical was transferred along the normal to the interface (*z*). The free energy profile is defined up to an arbitrary additive constant corresponding to the free energy of a reference state, which was chosen to be the water slab with the hydroxyl radical located in the gas phase. For this study, a somewhat smaller slab system with

[†] University of California, Irvine.

[‡] Pacific Northwest National Laboratory.

[§] Permanent address: Institute of Organic Chemistry and Biochemistry and Center for Complex Molecular Structures and Biomolecules, Academy of Sciences of the Czech Republic, Flemingovo n. 2, 16610 Prague 6, Czech Republic.

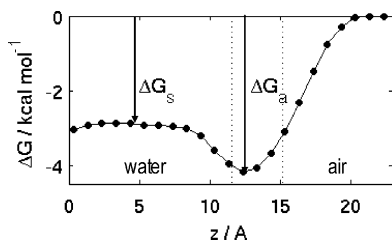


Figure 3. Free energy profile for transfer of an OH radical across the air–water interface. The interfacial region is indicated by the dotted lines. ΔG_s denotes the free energy of bulk solvation, and ΔG_a denotes the free energy of adsorption on the water surface.

600 water molecules in a $26.3 \times 26.3 \times 76.3$ Å simulation cell was employed.

The resulting free energy profile is shown in Figure 3. Our calculated value of the free energy of solvation, $\Delta G_s = -3.0 \pm 0.1$ kcal/mol, agrees well with the experimental value of $\Delta G_{s,\text{expt}} = -3.9 \pm 0.3$ kcal/mol.^{9,16,17} Because of its radical character, it is rather difficult to accurately describe the hydroxyl by a simple empirical force field. Yet, the good agreement between the calculated and experimental free energy of solvation, together with the satisfactory performance of the present force field in terms of OH microsolvation in water clusters,⁸ indicates that MD simulations with empirical potentials can provide a very useful insight into the processes at the air–water interface involving radicals.

In our experience, the free energy profile is very sensitive to the choice of the force field parameters in terms of the resulting ΔG_s . However, different OH parameters consistently yield a minimum of the free energy in the interfacial region that is about 1 kcal/mol lower than the free energy of the OH in the liquid phase,¹⁸ thus indicating a surface activity of OH radical. A careful analysis of MD trajectories revealed that OH in the bulk significantly perturbs the structure of water molecules in the first and second solvation shells relative to neat water, whereas at the surface this perturbation is absent. This provides evidence for the driving force behind the surfactant-like behavior of OH. It is interesting to note that polarizability does not play a significant role in the propensity of OH for the air–water interface,¹⁹ although it is crucial for reproducing the structures of small OH water clusters.⁸

On the basis of the analysis of the thermal accommodation of OH radical on the water surface as well as on the calculated free energy profile, we conclude that the mechanism by which a gas-phase OH becomes solvated in liquid water can be understood, in accord with the formulation of Wilson and Pohorille,²⁰ as capture by the surface with almost unit probability, followed by diffusion on the equilibrium free energy surface. Furthermore, as it is more favorable for the OH to be partially solvated at the surface rather than fully solvated in bulk water, surface activity of OH resulting in the partitioning of OH radicals between the surface and the bulk of liquid water is predicted. Under tropospheric conditions, the free energy difference of 1 kcal/mol between the surface adsorbed and fully hydrated OH corresponds to approximately 1 order of magnitude enhancement in the OH concentration at the interface of the aqueous droplets compared to the OH concentration in the

interior.⁸ This has some potentially important implications for heterogeneous reactions at the surfaces of aqueous atmospheric particles.⁸ Therefore, experimental validation of the predicted surface activity of OH radical is highly desirable. OH at the water surface could be in principle measured by the second harmonic generation technique, although it represents a rather challenging task.²¹ In any case, the chemical consequences of the possible surface enhancement of one of the most prominent atmospheric oxidants make this topic most interesting as well as highly relevant to explore.

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Supporting Information Available: Explanation of methods, computational details, and additional discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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