

Supplementary Material

Impact of cloud water droplets on OH production rate from peroxide photolysis

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SUMMARY

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1. Computational approach

The calculations have been carried out using a combined molecular dynamics and quantum mechanics approach. This approach is similar to that described in our previous work devoted to ozone photolysis at the vapor-liquid water interface.¹

Molecular dynamics simulations using a hybrid QM/MM force-field

Simulations have been carried out using the hybrid QM/MM approach^{2,3} developed in our group.⁴⁻⁷ The solute is described quantum mechanically (QM), the solvent is described classically using molecular mechanics (MM), and we allow for QM/MM electrostatic embedding. The simulations are done in the NVT ensemble (T=298K, Nosé–Hoover thermostat^{8,9}) using a box containing the solute and 499 water molecules. The box size is (in Å) 24.685 x 24.685 x 130. Periodic boundary conditions are used along the X and Y directions. The solute MHP is described at the B3LYP level¹⁰ using the 6-311+G(d) basis set.¹¹⁻¹³ Water molecules are described using the TIP3P model.¹⁴ We use the Gaussian 09 program¹⁵ for the QM calculations, Tinker 4.2¹⁶ for the MD simulations and the interface developed by the group of Nancy.¹⁷ The time step is 0.25 fs. After equilibration, the simulation is carried out for about 5.5 ns using a horsetail parallel sampling method.^{18,19}

Free energy calculations

The free energy profile for the accommodation process in Figure 1S has been calculated using the umbrella sampling²⁰ and WHAM^{21,22} methods. The reaction coordinate is the distance between the center of mass of the solute and the center of mass of the solvent. This distance is varied by steps of 0.25 Å. We assume a bias potential force constant $k=10 \text{ kcal/mol/Å}^2$. After thermalization (T=298K), we carry out a trajectory of 70 ps for each point along the reaction coordinate.

Calculation of the UV-Vis spectrum

From a QM/MM trajectory (93 ps) of MHP at the air-water interface, 370 snapshots were saved at regular intervals for further analysis. For each snapshot, the UV-Vis spectrum was calculated for MHP interacting electrostatically with the TIP3P water molecules that fall within a cutoff radius of 12.342 Å; water molecules in the snapshots beyond this radius are disregarded. We use the multi-reference configuration interaction (MRCI) method and the aug-cc-pVTZ basis set. The cross-section for a specific electronic transition is obtained through a Gaussian convolution using the expression:

$$\sigma(\nu) = 0.811 \times 10^{-12} \frac{f}{\Delta\nu_{1/2}} e^{-2.772 \left(\frac{\nu - \nu_0}{\Delta\nu_{1/2}} \right)^2}$$

where f is the oscillator strength for the electronic excitation energy ν_0 . Units of σ are $\text{cm}^2 \cdot \text{molecule}^{-1}$ if $\Delta\nu_{1/2}$ is expressed in cm^{-1} . We use $\Delta\nu_{1/2} = 4839 \text{ cm}^{-1}$. The cross-sections for the first five excited states have been added up. The final spectrum is obtained by averaging over the 370 snapshots. A similar calculation has been done for the isolated MHP to estimate the gas phase spectrum but using in this case a shorter trajectory (10 ps).

To account for errors in the COOH torsional angle distribution due to limited accuracy of the quantum mechanical method in the QM/MM simulations (B3LYP/6-311+G(d) level), the spectrum of each snapshot is multiplied by a weight factor estimated by the expression: $w = \exp(-\Delta E/RT)$, where $\Delta E = E(\text{QM}^2/\text{MM}) - E(\text{QM}^1/\text{MM})$, with $\text{QM}^2 = \text{CCSD(T)}/\text{aug-cc-pVQZ}$, $\text{QM}^1 = \text{B3LYP}/6-311+\text{G(d)}$ and $\text{MM}=\text{TIP3P}$.

The MRCI calculations with single and double excitations have been carried out with the ORCA program package.²³ All valence electrons were correlated, whereas the electrons of the 1s atomic orbitals from the oxygen and carbon atoms were frozen. The most important configurations were selected with a 10^{-6} hartree of cutoff threshold and the Davidson correction was applied to approximately account for higher excitations.

2. Figures

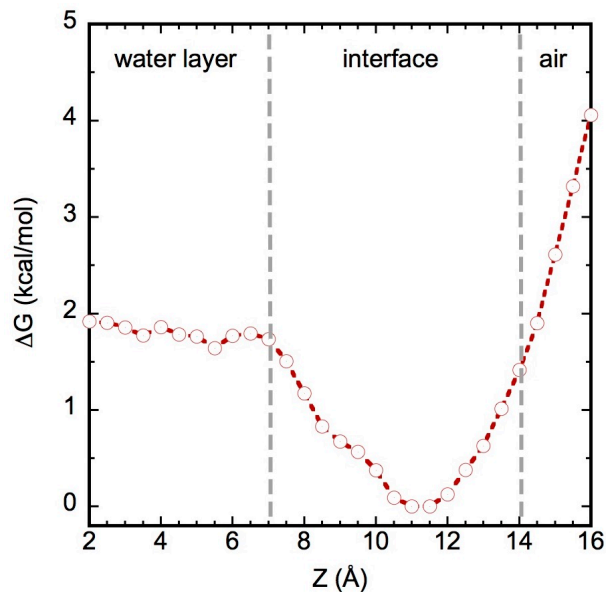


Figure S1. Free energy profile for MHP accommodation illustrating the high affinity of this peroxide for the air-water interface. Z is the distance between the MHP center of mass and the center of mass of the simulation box. The formal interface is at $Z=12$ Å. The average bulk/interface free energy difference is estimated here to $1.2 \text{ kcal}\cdot\text{mol}^{-1}$. We assume an interface width of 7 Å (between $7 \text{ Å} < Z < 14 \text{ Å}$) (see also Figure 1), which is close to the estimated width made in reference.²⁴ The calculations were carried out using QM/MM Molecular dynamics simulations at the B3LYP/6-311+G(d) level. The experimental free energy of solvation ($1\text{M}\rightarrow 1\text{M}$) for MHP is $-5.3 \text{ kcal}\cdot\text{mol}^{-1}$.²⁵

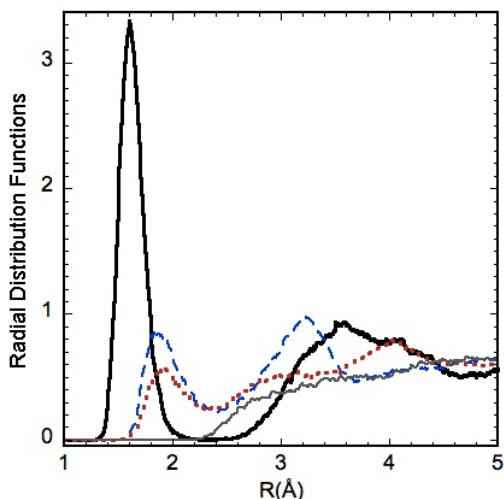


Figure S2. Solute-solvent radial distribution functions for MHP at the vapor-liquid water interface. They illustrate the formation of hydrogen-bonds between the O^aO^bH moiety of MHP and water molecules: $H-O_{\text{water}}$ (black), O^b-H_{water} (blue), O^a-H_{water} (red).

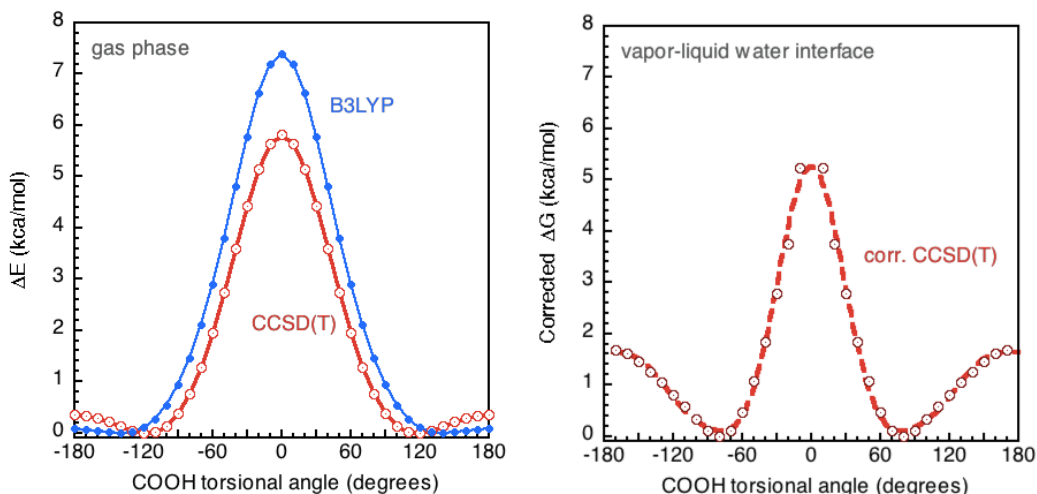


Figure S3. Calculated energy curves as a function of the COOH torsional angle in MHP. Left: potential energy in the gas phase. Right: corrected free energy at the vapor-liquid water interface. In the gas phase, the B3LYP curve (blue) corresponds to relaxed scan calculations at the B3LYP/6-311+G(d) level, while CCSD(T) (red) corresponds to single point CCSD(T)/aug-cc-pVQZ calculations on the preceding geometries. The free energy curve at the interface corresponds to an estimated CCSD(T)/aug-cc-pVQZ free energy profile; we use the approximation $\Delta G_{\text{interface}}(\text{CCSD(T)}) \approx \Delta G_{\text{interface}}(\text{B3LYP}) + \Delta E_{\text{gas}}(\text{CCSD(T)}) - \Delta E_{\text{gas}}(\text{B3LYP})$. The term $\Delta G_{\text{interface}}(\text{B3LYP})$ is obtained from the 5.5 ns simulation using the horsetail sampling method.

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