

Water enhancement of OH recycling pathways in isoprene oxidation

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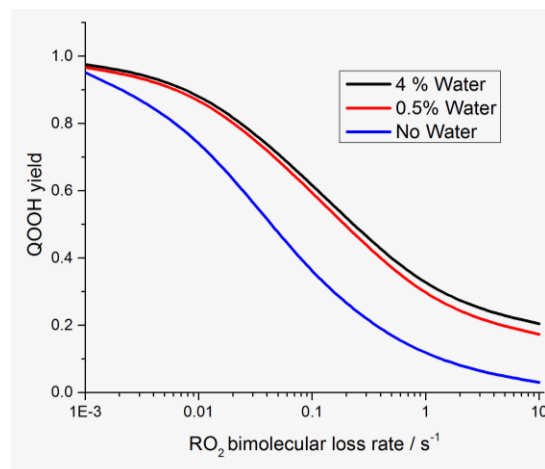
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Water can have a dramatic catalytic effect on gas phase chemical reactivity, lowering the energy of rate limiting transition states.¹ and impacting absorption cross-sections.² The atmospheric importance of such mechanisms has been noted,³ however there remain many important atmospheric reactions for which the role of water complexes is yet to be studied in detail.

Isoprene is a key biogenic compound emitted from plants, whose oxidation chemistry remains unresolved. Current modeling efforts underpredict the amount of [OH] observed near tropical forests by up to an order of magnitude. The ratio of observed [OH] to modeled [OH] appears to correlate strongly with ambient isoprene concentrations, suggesting an efficient OH recycling channel.⁴ Previous workers have carried out detailed studies on the mechanism of isoprene oxidation, providing extensive maps of the relevant potential energy surface stationary points.⁵ OH recycling is understood to be largely controlled by whether important peroxy (RO₂) radicals formed in the oxidation process can isomerise to QOOH before being intercepted by atmospheric species such as NO and HO₂.

We have investigated the extent to which water complexes might accelerate important isomerisation steps in isoprene oxidation, and whether the inclusion of these pathways in isoprene oxidation kinetic models might help reconcile the discrepancy between the observed and modelled [OH]. We have carried out calculations at the M06-2x/6-311+G(2df,3pd)//CCSD(T)-f12b/aug-cc-pVDZ level of theory, both with and without water. Our findings indicate that a single water molecule decreases the barrier of an important isomerisation transition state by 5.5 kcal mol⁻¹. Explicitly coupled master equation simulations and numerical modelling studies of the full isoprene + OH + O₂ (+ H₂O) system suggest that the presence of water enhances OH recycling isomerization channels along the lines shown in the figure.



References

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