

Evaluating condensation-relevant properties of terpene oxidation products using COSMOTerm

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A combination of statistical thermodynamics methodology with relatively simple quantum-chemical molecular data has proven useful for exploring the properties of compound types for which experimentally measured properties are scarce. We have recently applied the COSMO-RS approach, as implemented in the COSMOTerm program, to explore the saturation vapor pressures and Henry's law constants of potential products formed in both sequential and peroxyradical-based autoxidation of alpha-pinene (with either O₃ or OH as the initiating oxidant), as well as to evaluate Setschenow constants for a large range of atmospherically relevant solute-salt combinations. Comparison to experimental data on a limited set of related compounds indicates that while these COSMOTerm results are far from quantitative, the predictions are systematic. For example, saturation vapor pressures are likely overestimated by up to one order of magnitude per intramolecular hydrogen bond even with the newest and highest-level parameterizations available, while Setschenow constants are systematically biased toward greater salting out. Nevertheless, COSMOTerm allows us to make useful order-of-magnitude predictions of both saturation vapor pressures, solubilities and salting behavior for systems for which no other modelling method is currently applicable. For example, our calculations strongly suggest that products of OH – initiated monoterpene autoxidation have significantly lower volatilities than the corresponding products of O₃ – initiated autoxidation with identical numbers of carbon and oxygen atoms.

Isoprene dihydroxy dihydroperoxide (ISO(POOH)2) provides a useful test system for evaluating volatility predictions of autoxidation products. ISO(POOH)2 contains four hydrogen-bonding functional groups, and saturation vapor pressure has recently been experimentally estimated to be about 1E-9 bar. While being chemically representative of larger (e.g. monoterpene) autoxidation products, the molecule is also small enough that all conformers of all structural and stereoisomers (about 70 000 in total) can be explicitly simulated. COSMOTerm-predicted saturation vapor pressures for the atmospherically dominant structural isomer of are 1-2 orders of magnitude larger than the experimental estimate, consistent with an overestimation of a factor of 2-3 for each of the four intramolecular H-bonds. Unfortunately, test calculations also demonstrate that the default conformational sampling method implemented in the COSMOconf module is inappropriate for the ISO(POOH)2 system, as the predicted saturation vapor pressure varies by up to a factor of 40 depending on the arbitrary input conformer. We also find large differences (up to a factor of 100) in saturation vapor pressures between stereoisomers, as well as between structural isomers, where the OH and OOH groups are located on different carbon atoms. For example, isomers with OOH groups on adjacent carbon atoms tend to have lower saturation vapor pressures, likely because of steric strain preventing efficient intramolecular H-bonding.