Tuning the $^1O_2$ Oxidation of a Phenol at the Air/Solid Interface of a Nanoparticle: Hydrophobic Surface Increases Oxophilicity

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ABSTRACT

Although silica surfaces have been used in organic oxidations for the production of peroxides, studies of airborne singlet oxygen at interfaces are limited and have not found widespread advantages. Here, with prenyl phenol coated silica and delivery of singlet oxygen ($^1O_2$) through the gas phase, we uncover significant selectivity for dihydrofuran formation over allylic hydroperoxide formation. The hydrophobic particle causes prenyl phenol to produce an *iso*-hydroperoxide intermediate with an internally protonated oxygen atom, which causes elimination of H_2O_2 in its activity. Dihydrobenzofuran and H_2O_2 are being quantitated and analyzed using NMR. In contrast, hydrophilic particles cause prenyl phenol to produce allylic hydroperoxide, due to phenol OH hydrogen bonding with SiOH surface groups. Mechanistic insight is provided by air/solid interface total rate constants measurements (*ASI-*k_T) of $^1O_2$ are determined on hydrophobic and hydrophilic particles coated with the prenyl phenol. A slope intersection method (SIM) method was also developed that uses the airborne $^1O_2$ lifetime ($\tau_{airborne}$) and surface-associated $^1O_2$ lifetime (τ_{surf}) to quantitate $^1O_2$ transitioning from volatile to non-volatile and surface boundary (surface$\cdots^1O_2$). Further mechanistic insight on the selectivity of the reaction of prenyl phenol with $^1O_2$ was provided by DFT calculations.