

2.127 An experimental study on carbocationic oligomerization processes of VOCs at acidic water surfaces.

Early Career Scientist

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Abstract:

Recent field and experimental studies show that atmospheric particles are sufficiently acidic to trigger carbocationic chain reactions at their surfaces. Electrophilic attack of interfacial H_3O^+ to volatile organic compounds (VOCs) induces carbocationic chain reactions including oligomerization at the surfaces, which are to play key roles in the evolution of atmospheric particles. Here we studied oligomerization abilities of various unsaturated hydrocarbons and competing chain reactions at the water surface as an analogue of atmospheric particles, by direct detection of carbocations using an experimental system equipped with online mass spectrometry of microjets. After ~ 10 us exposure of the reactant gases to the acidic water surface ($1 \leq \text{pH} \leq 5$), proton-transfer reaction from H_3O^+ to the reactant molecules were observed, initiating competing chain reactions of chain-propagation, chain-transfer and hydride(H^-)-abstraction. The oligomerization abilities of the monomers were varied with the relative efficiency of chain-propagation to competing reactions and are enhanced when (1) pi-electron at the reactive C=C bond of a nucleophile is enriched by electron-donating functional group and (2) carbocation acting as an electrophile shows conjugative resonance. This resulted in the largest oligomer formation of isoprene up to the decamer, which is almost the limit of diffusion-controlled growth. Notably, conjugative resonance is known to restrain the oligomerization in the bulk organic solutions, implying that the water surface is a distinct reactor from the bulk. We found that even relatively unreactive monomers propagate to the oligomer, via hydride-abstraction and subsequent pi-alkylation. Furthermore, co-oligomerization is found to assist the chain-growth of the solely ineffective monomers when reactive species are co-existing (e.g., reactive isoprene and inert 1-pentene). These results consistently show that unsaturated hydrocarbons easily get protonated and form oligomeric-products at acidic water surfaces while the competition between chain-propagation, chain-transfer and hydride-abstraction determines the growth pathway of the interfacial carbocation.