

## What factors control the oligomerization of volatile organic compounds on atmospheric particles?

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Recent field and experimental studies show that atmospheric particles are sufficiently acidic to trigger acid-catalyzed reactions (Enami et al., 2012; Guo et al., 2016; Liggio et al., 2007). Although the uptake of volatile organic compounds (VOCs) and their oligomerization on the acidic surfaces would play important roles in the growth of atmospheric particles, the mechanism still remains elusive. Here we examined reactive uptake and the oligomerization ability of acyclic and cyclic VOCs (isoprene, 1,3-butadiene, 1,4-pentadiene, 1-pentene, 2-pentene, cyclohexene, 3-methylcyclohexene, 1-methylcyclohexene, 4-methylcyclohexene, 1,3-cyclohexadiene and 1,4-cyclohexadiene) exposed to an acidic water microjet of bulk pH ranging from 1 to 5. Cationic products are generated on the surface within ~10 micro seconds, that are directly detected using surface-sensitive mass spectrometry. We found that the oligomerization ability largely depends on the structure. The oligomer length of the acyclic VOCs follows the order: isoprene >> 1,3-butadiene > 1,4-pentadiene >> 1-pentene ~ 2-pentene. The cationic oligomerization of isoprene affords the decamer (a C<sub>50</sub> product at m/z 681.6), while 1-pentene/2-pentene remain as monomers, implying that oligomerization is facilitated by (1) resonance stabilization through the formation of a tertiary carbocation with a conjugated double bond pair and (2) pi-electron enrichment induced by the neighboring methyl group. We conclude these factors make isoprene the best nucleophile among a series of acyclic VOCs for successful oligomerization on the acidic water surface. We found the oligomerization ability of cyclic VOCs is similarly controlled by these factors. The atmospheric implication will be discussed in the presentation.

Enami, S., Mishra, H., Hoffmann, M. R., & Colussi, A. J. (2012). Protonation and oligomerization of gaseous isoprene on mildly acidic surfaces: Implications for atmospheric chemistry. *Journal of Physical Chemistry A*, 116(24), 6027–6032. <https://doi.org/10.1021/jp2110133>

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