

## Acid-catalyzed reactions of limonene and terpineol and their implication in secondary organic aerosol (SOA) formation

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It has been reported that acid-catalyzed reactions of some semi-volatile organic compounds can affect their partitioning between the gas phase and the particle phase, hence the properties of atmospheric particles. These particle-phase reactions can enhance secondary organic aerosol (SOA) formation via accretion reactions including polymerization, aldol condensation etc. (Jang et al., 2003; Liggió & Li, 2008) and addition reactions (Surratt et al., 2007) such as organosulfate formation from volatile/semi-volatile organics (e.g. carbonyls, alcohols and alkenes). Other studies, however, found that acid-catalyzed reactions are either thermodynamically unfavourable (Basanti & Pankow, 2004) or kinetically too slow (Zhao et al., 2004) to contribute to substantial amount of SOA formation in the troposphere. The discrepancy is largely due to the fact that both mechanisms and kinetics for those acid-catalyzed reactions are still unclear, and even the product identities of which remain poorly understood.

In the present study, we investigated the acid-catalyzed reactions of biogenic volatile organic compounds by a flow cell reactor with acidic particles deposited onto a hydrophobic substrate. Limonene (LN) and a mixture of terpineols (3 isomers of limonene hydroxyls, TL) were used as the model VOC compounds to study the acid-catalyzed reactions. Reaction products were identified from experiments under different acidity conditions by controlling the relative humidity (RH). For both LN and TL experiments, limonene dimers (LND) and limonene trimers (LNT) were formed under low RH conditions (<20%) and high VOC concentration level (~30 ppmv for LN and ~1 ppmv for TL). At lower VOC concentrations (~1 ppmv for LN and ~0.1 ppmv for TL), dimer and trimer formation for LN experiments was less significant (only found in 2% RH conditions), while dimers and trimers were still observable in TL experiments at RH=2% and 20%. A limonene ketone (carvenone, LNK) was also observed in most of the low RH experiments with LN or TL. The amount of these products (LND, LNT and LNK) increased with decreasing RH. Under higher RH conditions (>20%), both LN and TL gave monomer derivatives as the reaction products, i.e., several unidentified monomers (probably carboxylic derivatives of limonene, LNM) for LN or limonene

dihydroxyls (LNOH2) for TL. The formation of these monomer derivatives was also dependent on RH, with increasing amounts of products formed at higher RH conditions. The acidity-dependent reaction pathways (Fig. 1) were proposed based on product information from the flow cell reactor experiments and bulk solution experiments.

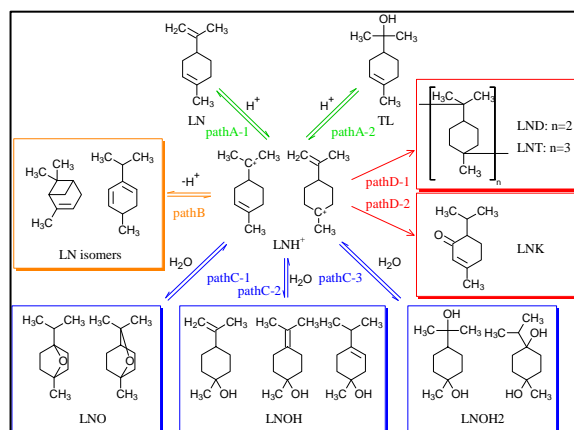


Fig. 1 Acidity-dependent reaction pathways of limonene (LN) and terpineols (TL). Products are shown by typical structures while isomers of them were also observed in the experiments.

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