# Acid-catalyzed condensed-phase reactions of limonene and terpineol and their impacts on gas-to-particle partitioning in the formation of organic aerosols

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# 1. Schematic of the flow cell reactor



FIGURE S1 Schematic of the setup for the gas-particle (GP) experiments.

ovnt <sup>a</sup>	DCCAD	VOC and concentration <sup>d</sup>		rxn	particle composition and estimated mass <sup>e</sup>								
expt	<b>D</b> 5-5A	voc a			time	A/S <sup>f</sup>	mass <sup>g</sup>	A/S	mass	A/S	mass	A/S	mass
	%	VOC	ppm	mg/m <sup>3</sup>	hr		mg		mg		mg		mg
BS-1	17.6 wt	LN			24	0.0							
BS-2	32.5 wt	LN			24	0.0							
BS-3	46.3 wt	LN			24	0.0							
BS-4	57.8 wt	LN			24	0.0							
BS-5	17.6 wt	TL			24	0.0							
BS-6	32.5 wt	TL			24	0.0							
BS-7	46.3 wt	TL			24	0.0							
BS-8	57.8 wt	TL			24	0.0							
	GP-RH <sup>c</sup>												
GP-1	1.7	LN	30	170	24.3	0.0	1.2	0.2	1.1	0.4	0.9	0.8	0.5
GP-2	8.7	LN	31	170	24.5	0.0	1.4	0.2	1.3	0.4	1.1	0.8	0.4
GP-3	18.2	LN	38	210	24.0	0.0	1.5	0.2	1.4	0.4	1.3	0.8	0.4
GP-4	35.3	LN	37	210	24.0	0.0	1.8	0.2	1.7	0.4	1.6	0.8	1.5
GP-5	62.2	LN	34	190	24.3	0.0	2.4	0.2	2.3	0.4	2.2	0.8	1.9
GP-6	1.8	LN	1.1	5.8	24.0	0.0	1.2	0.2	1.1	0.4	0.9	0.8	0.5
GP-7	18.2	LN	1.1	5.8	24.3	0.0	1.5	0.2	1.4	0.4	1.3	0.8	0.4
GP-8	62.6	LN	1.1	6.0	24.0	0.0	2.4	0.2	2.3	0.4	2.2	0.8	1.9
GP-9	8.5	LN	0.9	4.8	72.0	0.0	1.4						
GP-10	2.2	TL	1.2	7.7	24.0	0.0	1.2	0.2	1.1	0.4	0.9	0.8	0.4
GP-11	18.4	TL	1.3	7.9	24.3	0.0	1.5	0.2	1.4	0.4	1.3	0.8	0.4
GP-12	59.9	TL	1.3	7.8	24.0	0.0	2.3	0.2	2.2	0.4	2.1	0.8	1.8
GP-13	1.4	TL	0.08	0.51	24.0	0.0	1.2	0.2	1.1	0.4	0.9	0.8	0.5
GP-14	18.8	TL	0.13	0.82	24.6	0.0	1.5	0.2	1.4	0.4	1.3	0.8	0.4
GP-15	59.8	TL	0.23	1.4	24.3	0.0	2.3	0.2	2.2	0.4	2.1	0.8	1.8

TABLE S1. Experimental conditions for the bulk solution	(BS) and gas	s-particle (GP)	experiments
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Notes:

a: Experiment number. BS: bulk solution experiments; GP: gas-particle experiments.

b: Weight percentage (wt%) of sulfuric acid in bulk solution (BS) experiments.

c: Relative humidity (RH, %) in gas-particle (GP) experiments.

d: VOC vapor used in gas-particle (GP) experiments and their concentrations in units of ppm and µg/m<sup>3</sup>. LN: limonene; TL: terpineol.

e: Particle composition as sulfuric acid (SA) only or sulfuric acid (SA)/ammonium sulfate (AS) mixtures in gas-particle (GP) experiments. All GP experiments used 9 µmole of SA or SA/AS in terms of sulfate ion. The amounts of ammonium ion varied from 0 to 7.2 µmole.

f: Molar ratio of ammonium ion (A) to sulfate ion (S).

g: Total mass of inorganic components in the particle phase predicted by E-AIM model (*1*). All GP experiments used 9  $\mu$ mole of SA or SA/AS in terms of sulfate ion, while the amounts of ammonium ion varied from 0 to 7.2  $\mu$ mole. The masses of the species (H<sup>+</sup>, OH, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>-2</sup>, HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>O) were added up to obtain the total mass of the particles. Bold numbers are extrapolated (6-order polynomial fit) values as E-AIM model cannot give calculations for RH<10%.

## 3. Chromatograms of products in the BS experiments and mass spectra of typical products

TICs of typical products from the bulk-solution (BS) experiments are shown in Figure S2. Typical EI spectra of LNM, LNK, LND and LNT are shown in Figures S3-S7. It is worth noting that there are two strong peaks indicating LN dimeric structures (with MW 268) in the GP experiments under 8.7 % RH (retention times 20.59 and 20.78 min, Fig. 1-b). From the fingerprint fragments of m/z 77, 91 and 105 (Figure S5), it was suggested that these two compounds are aromatic isomers, although this attribution should be regarded as tentative since authentic standard reference is absent. These dimeric products have molecular weight of 268 Da and are 4 Da less than 2 limonene molecules (272 Da), suggesting that inter-molecular hydrogen shift and disproportionation might have happened in their formation. In fact, there are some synthetic studies showing that this process can occur under acidic conditions (2). Although buried in the messy peaks in the LND region, these peaks were also observed in GP-LN experiments at RH 1.7% (Figure 1), which is consistent with our previous study in which aromatic products were formed at extremely low RH conditions with octanal as the VOC (*3*).



FIGURE S2. Chromatograms of products in the bulk solution (BS) experiments. From top to bottom: sulfuric acid concentrations 57.8, 46.3 and 32.5 wt%. LNO: limonene oxides (see detailed descriptions in Table 1 and typical structures and IUPAC nomenclatures in Figure S8); LNOH: limonene hydroxyls (see detailed descriptions in Table 1 and typical structures and IUPAC nomenclatures in Figure S8); LNOH2: limonene dihydroxyls (see detailed descriptions in Table 1 and typical structures and IUPAC nomenclatures in Figure S8); LNOH2: limonene dihydroxyls (see detailed descriptions in Table 1 and typical structures and IUPAC nomenclatures in Figure S8); LND: limonene dimeric products and their derivatives (see detailed descriptions in Table 1).



FIGURE S3. Mass spectrum of LNK



FIGURE S4. Mass spectrum of LNM



FIGURE S5. Mass spectrum of LND with m/z 268



FIGURE S6. Mass spectrum of LND with m/z 272



FIGURE S7. Mass spectrum of LNT

4. Typical structures and nomenclatures of some products



LN

# LNOH



#### FIGURE S8. Typical structures, and the numberings and nomenclatures of the reactants

and products

## 5. Semi-quantification

Table S2 shows the response factors in GC-MS analysis with peak areas of the products from TICs divided by those of the internal standard (hexadecane) as the "relative intensities". As shown in Table S2, the response factors of the standards for the monomers LN, LNO, LNOH and LNOH2 ranged from 3315 to 3760, with the intercepts very close to zero. Also shown is the trend that the greater the number of functional groups, the lower the response factors, except for 1,8-cineole as the epoxy group it possesses is much less polar than the hydroxyl groups in other oxygenated products (LNOH and LNOH2). Therefore, one would expect an uncertainty of 10-15% if a single response factor between 3310-3760 (for example 3500) is used to quantify the monomer products (LNO, LNOH and LNOH2). Although the single response factor approach was not used for our semi-quantification of monomers (LNO, LNOH, LNOH2, LNK and LNM etc.), it was used for dimeric and trimeric products (LND and LNT), as the structures of these dimeric and trimeric products are mostly unknown.

The response factor for cembrene ( $C_{20}H_{32}$ ) was 6120 (approximately two times of that of limonene) and was used to represent those of diterpenes, which possess a carbon number two times that of limonene. Although the MS detector does not measure the "effective carbon numbers" as does the flame ionization detector (FID) and cannot be treated as if the response factor is proportional to the carbon number of the analytes, this assumption will be reasonable given that the analytes are similar in structure and have similar functional groups, which is true for our case (double bonds and hydroxyl groups mainly). For the hydroxylated derivatives of diterpenes, we expect that the response factors of those hydroxylated products are smaller than 6120. Overall, we chose 6000 for all the dimeric products (LND) and expect an uncertainty of around 20%. Similarly, we chose a response of 9000 for trimeric products (LNT). As the response factors for hydroxylated LND and LNT would lie in the lower end of the estimated range, our calculations most probably

underestimate the amounts of LND and LNT, which is a significant source of the estimated uncertainty of 20%.

The estimation of  $H^*$  and  $K_{p,rxn}$  was based on these semi-quantification results, which were subjected to an error of around 20% due to surrogates being used and an uncertainty of around 30% from triplicate runs of selected samples (error bars in Figure 2 in the paper).

TABLE	S2. I	Fitting	para	ameters	of	standards	for	
semi-qua	ntificati	on						
y=Bx+A (y: relative intensity to 0.025 g/L hexadecane)								
Name	В		A	Compo	ind			
LN	3725.4	4 -(	0.3	Limonene				
LNO	3759.9	9 -(	0.3	Limonene oxides				
LNOH	3603.0	6 -(	0.4	Limonene hydroxyls				
LNOH2	3314.	5 -(	0.5	Limonene dihydroxyls				
CB	6120.	3 -(	0.3	Cembre	ne			

# 6. The apparent Henry's law constants (H<sup>\*</sup>) from BS experiments

The apparent Henry's law constant  $(H^*)$  in this study was estimated from the results of the BS experiments, assuming that the gas phase concentration of LN or TL was at their saturated vapor pressures (4) as the amounts added exceeded their solubility:

$$H^{*} = \frac{C_{\text{tot.}}}{p_{\text{LN/TL}}} = \frac{C_{\text{LN/TL}} + C_{\text{LNO}} + C_{\text{LNOH}} + C_{\text{LNOH2}}}{p_{\text{LN/TL}}},$$
(1)

where  $C_{LN/TL}$  is the equilibrium concentration of LN or TL (mol/L);  $C_{LNO}$ ,  $C_{LNOH}$  and  $C_{LNOH2}$  are the equilibrium concentrations of LNO, LNOH and LNOH2 respectively (mol/L);  $p_{LN/TL}$  is the saturated vapor pressure of LN or TL, i.e. 0.001875 atm for LN (5) and 0.0000526 atm for TL (6) at 298K.

As shown in Table S3, the H<sup>\*</sup> values for LN under acidic conditions (17.6~46.3 wt% sulfuric acid) ranged from  $2.1 \times 10^{-2}$  to  $4.0 \times 10^{-2}$  M/atm in the same magnitude as the literature values that were determined under neutral conditions (7, 8). The actual H<sup>\*</sup> value for the 57.8 wt% sulfuric acid concentration condition should be higher than our estimation (4.6×10<sup>-2</sup> M/atm) due to dimeric product formation (see the section on product formation in the text and Figure S2), which was not included in

our calculations. The H<sup>\*</sup> values of TL, however, were lower than the literature value of a compound (linalool) with a similar structure (8) by 1~2 orders of magnitude (Table S3), although they increased slightly as the acid concentration increased. For compounds with a hydroxyl group, such as TL, protonation increased the solubility in the acidic aqueous phase while the "salting-out effect" decreased the solubility (8). It is difficult at this point to determine which effect dominates. Nevertheless, the estimated apparent Henry's law constants for LN and TL did not increase under mildly acidic conditions (sulfuric acid concentrations <50 wt%), which suggests that hydration alone (without oligomerization) under acidic conditions cannot lead to an increase in partitioning to the particle phase beyond that measured under neutral conditions.

TABLE S3. Estimated apparent Henry's law constant (H*) of LN from the bulk solution (BS) experiments. <sup>*</sup> Dimeric compounds formed under these conditions were not included						
VOC	H <sub>2</sub> SO <sub>4</sub> conc. (wt%)	H or H <sup>*</sup> (mol/L/atm)	Reference			
LN	0	3.6×10 <sup>-2</sup>	(8)			
LN	0	$4.4 \times 10^{-2}$	(7)			
LN	17.6	2.1×10 <sup>-2</sup>	Current study			
LN	32.5	$2.5 \times 10^{-2}$	Current study			
LN	46.3	$4.0 \times 10^{-2}$	Current study			
LN	57.8	$4.6 \times 10^{-2^*}$	Current study			
TL	0	39	(8)			
TL	17.6	0.76	Current study			
TL	32.5	0.88	Current study			
TL	46.3	1.4	Current study			
TL	57.8	$1.7^{*}$	Current study			

7. Product (LND and LNOH2) amounts vs. reaction time (Figure S9)



FIGURE S9. Relative abundance of LND (cationic polymerization product) and LNOH2 (hydration product) as a function of reaction time in GP experiments using terpineol (TL) as the VOC to react with sulfuric acid particles under 10% RH.

#### 8. Literatures cited

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