Supporting Information

Photosensitized formation of secondary organic aerosols above the air/water interface

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Mechanism formation of VOCs and SOA precursors. The mechanistic pathways leading to the observed gas phase products from an NA-HA system is described briefly. As a photosensitizer i.e., humic acid, gets excited upon absorption, a variety of reactive species may be produced in the aqueous solution (e.g., OH, ^{3}HA*, $^1O_2$, O_2^- or e_{aq}^-), initiating various photochemical degradation pathways.[1,2] In the presence of nonanoic acid, excited HA initiated the photodegradation via hydrogen abstraction,[3] possibly directly from the humic acid triplet state (^{3}HA*). This leads to the formation of an α-carboxyalkyl radical (R-CHCOOH). Further addition of O_2 led to the formation of a α-peroxyl carboxylic acid (R-CH(O_2)COOH). Subsequent chemistry of this radical via multiple oxidation steps implied either the degradation of the initial molecule leading to smaller products or a conservation of the carbon skeleton leading to polyoxygenated compounds. Both routes will lead to the formation of the identified products in the gas phase (i.e., saturated aldehydes (C_7-C_9), saturated acids (C_5-C_8), etc.), corresponding to classical oxidative chemistry. As identified by Ciuraru et al.[4] for nonanoic acid and Fu et al.[5] for octanol, the fact that surfactants are enriched at the interface facilitated a few pathways in addition to the oxidative chemistry mentioned above. Namely, at the interface, the α-carboxyalkyl radical may undergo disproportionation or dimerization in the presence of another such radical and addition of O_2, forming as expected a α-peroxyl carboxylic acid (see Figure 3). The disproportionation of the α-carboxyalkyl radical yielded an unsaturated product and the original acid as products. The location of the unsaturation will depend upon the location of the carbon on which the H-abstraction took place. In the case of nonanoic acid, it is highly probable that it takes place in α position to the carboxylic function,

producing nonenoic acid. The formation of unsaturation via elimination of HO_2 from the α-carboxyalkyl radical is in principle also possible, but for octanol, it is probably too slow at room temperature as this channel is quite endothermic.[5] Following the production of these first-generation products, similar radical reactions may take place, producing 2nd generation products, and so on. Likewise, radical recombination gives branched compounds, producing the identified unsaturated products (i.e., unsaturated aldehydes (C_6-C_9), unsaturated acids, etc.). The formation of dienes and polyalkenes as possible candidates for SOA precursors due to their high reactivity with ozone would be explained by further H-abstraction from the α-position of the double bond. This abstraction pathway would be favored thermodynamically due to high electron delocalization and a more stabilized radical due to resonance.

Although disproportionation and O_2 addition are strongly exothermic, one expects that the likelihood of the disproportionation increases as the local concentration of radicals becomes large, for example, under our conditions of continuous illumination with constant regeneration of the photosensitizer. The availability of oxygen molecules from the gas phase certainly helps to promote the oxygen addition reaction at the air interface, providing a ready source of peroxy-alcohol radicals. Altogether, this promotes chemical cycling at the interface, with unsaturated products arising from the nth generations, that could all react with ozone and act as a source of SOA.

Table S1. List of volatile organic compounds (VOC) identified by PTR-ToF-MS (using H_3O^+ as ionization source) during the photochemistry of nonanoic acid (NA) in the presence of humic acid (HA) and the subsequent dark ozone reaction.

Class of compounds	Volatile organic compounds	Protonated ion	Exact masses [m/z]
Saturated aldehydes	Hexanal	$C_6H_{13}O^+$	101.09608
	Heptanal	$C_7H_{15}O^+$	115.11174
	Octanal	$C_8H_{17}O^+$	129.12740
	Nonanal	$C_9H_{19}O^+$	143.14304
Unsaturated aldehydes	Pentenal	$C_5H_9O^+$	85.0648
	Hexenal	$C_6H_{11}O^+$	99.08044
	Heptenal	$C_7H_{13}O^+$	113.09608
	Octenal	$C_8H_{15}O^+$	127.11174
	Nonenal	$C_9H_{17}O^+$	141.12740
Saturated acids	Pentanoic acid	$C_5H_{11}O_2^+$	103.0753
	Hexanoic acid	$C_6H_{13}O_2^+$	117.09100
	Heptanoic acid	$C_7H_{15}O_2^+$	131.1070
	Octanoic acid	$C_8H_{17}O_2^+$	145.1228
Unsaturated acids	Pentenoic acid	$C_5H_9O_2^+$	101.05968
	Hexenoic acid	$C_6H_{11}O_2^+$	115.07536
	Heptenoic acid	$C_7H_{13}O_2^+$	129.09100
	Octenoic acid	$C_8H_{15}O_2^+$	143.10666
	Nonenoic acid	$C_9H_{17}O_2^+$	157.12200
Alkanes	Hexane	$C_6H_{15}^+$	87.1170
	Heptane	$C_7H_{17}^+$	101.1330
	Octane	$C_8H_{19}^+$	115.1480
	Nonane	$C_9H_{21}^+$	129.16400
Alkenes	Pentene	$C_5H_{11}^+$	71.0855
	Hexene	$C_6H_{13}^+$	85.10118
	Heptene	$C_7H_{15}^+$	99.11684
	Octene	$C_8H_{17}^+$	113.1330
	Nonene	$C_9H_{19}^+$	127.1480

Dienes	Hexadiene	$C_6H_{11}^+$	83.08553
	Heptadiene	$C_7H_{13}^+$	97.101181
	Octadiene	$C_8H_{15}^+$	111.11681
	Nonandiene	$C_9H_{17}^+$	125.1330
Terpenes	Isoprene	$C_5H_9^+$	69.0698
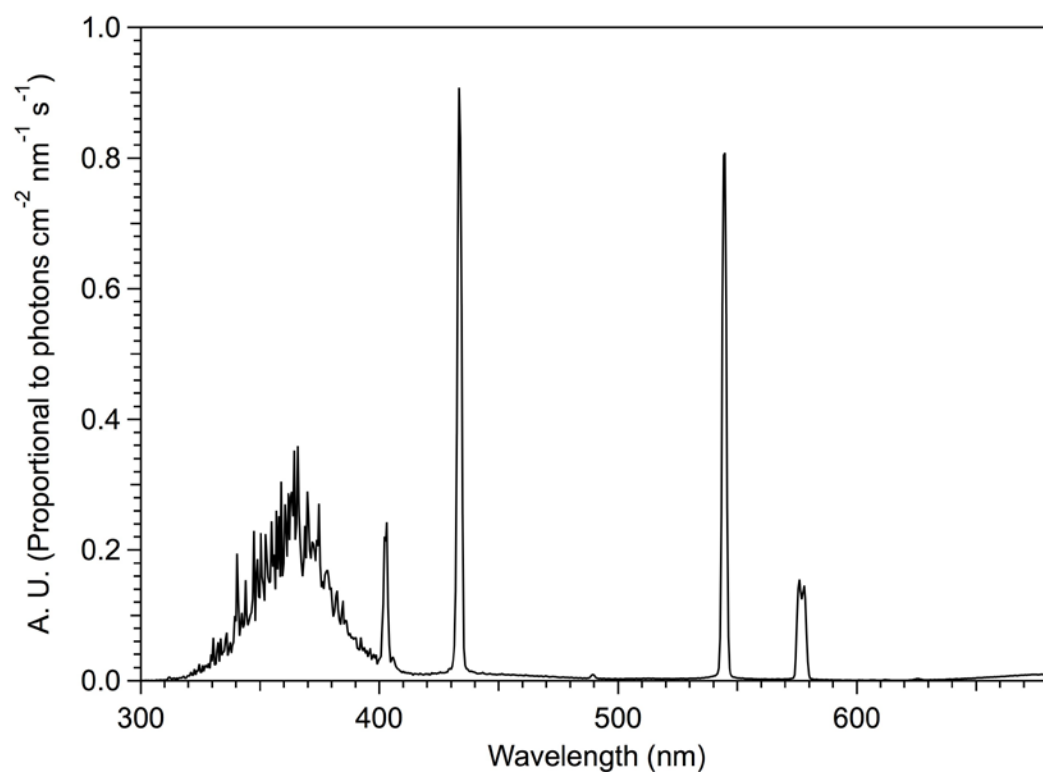
Figure S1. Irradiation spectrum of the lamps used for air-sea interface experiments.
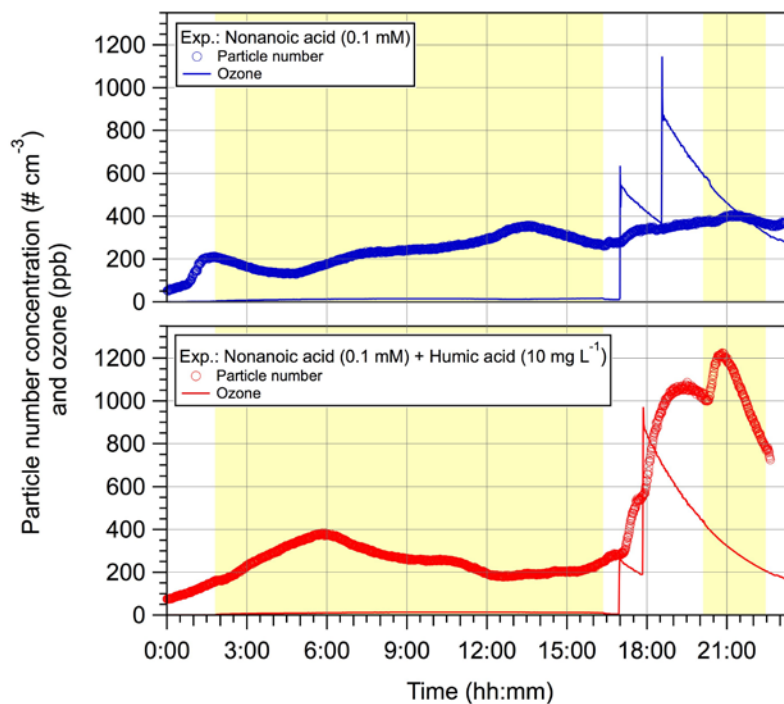
Figure S2. Comparison of particle formation measured with the ultrafine condensation particle counter from multiphase simulation chamber experiments conducted in the presence of humic acid (HA) and nonanoic acid (NA) (Exp. 2 in Table 1) compared to nonanoic acid (NA) only (Exp. 3 in Table 1). The yellow part represents the periods when the lights were on.
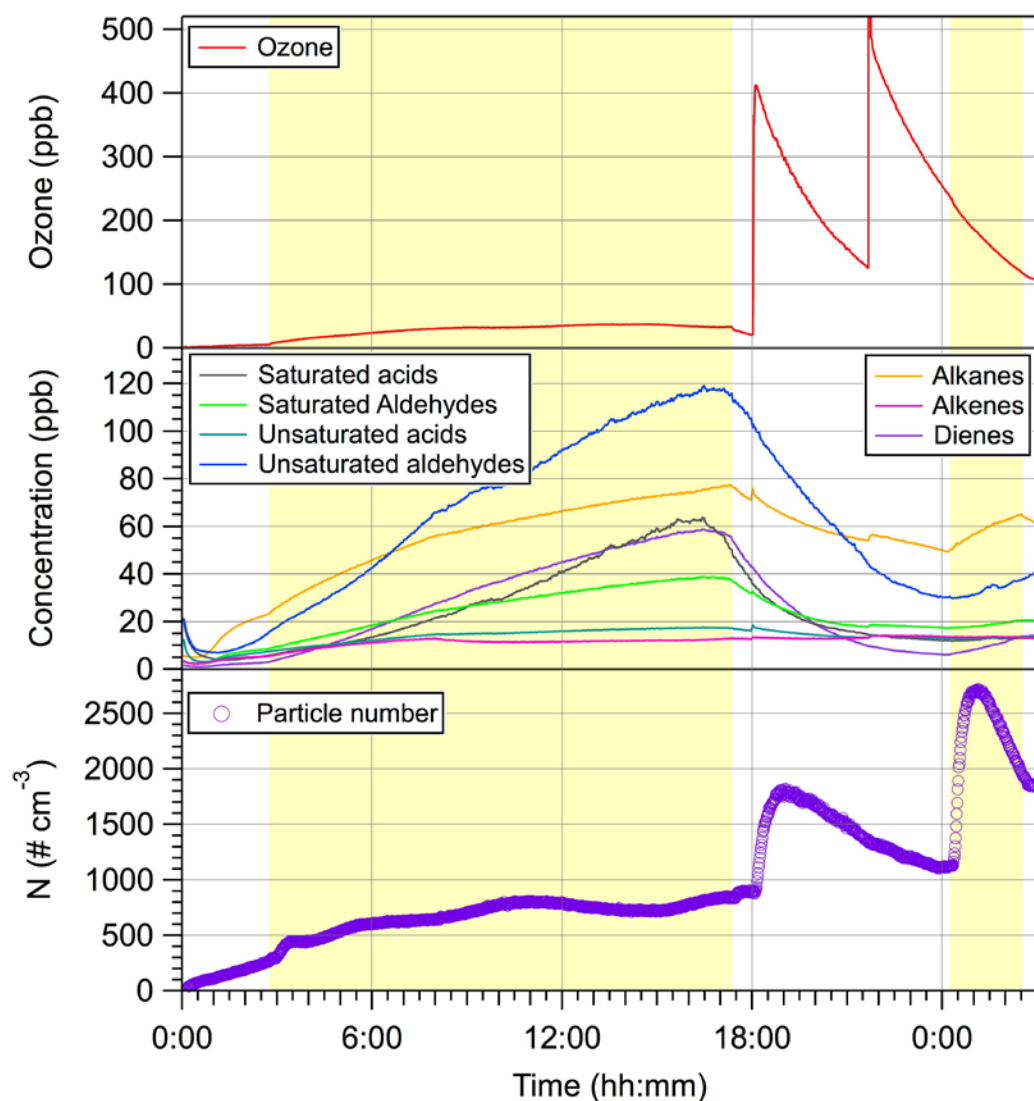
Figure S3. Multiphase simulation chamber experiments conducted in the presence of ([HA] = 10 mg L^{-1} and NA = 1 mM). Top graph: time-concentration profile of ozone; Middle graph: time concentration profiles of VOC identified and measured by the PTR-ToF-MS; Bottom graph: Particle number concentration measured with the ultrafine condensation particle counter. The yellow part represents the period when the lights were on (Exp. 9 in Table 1).
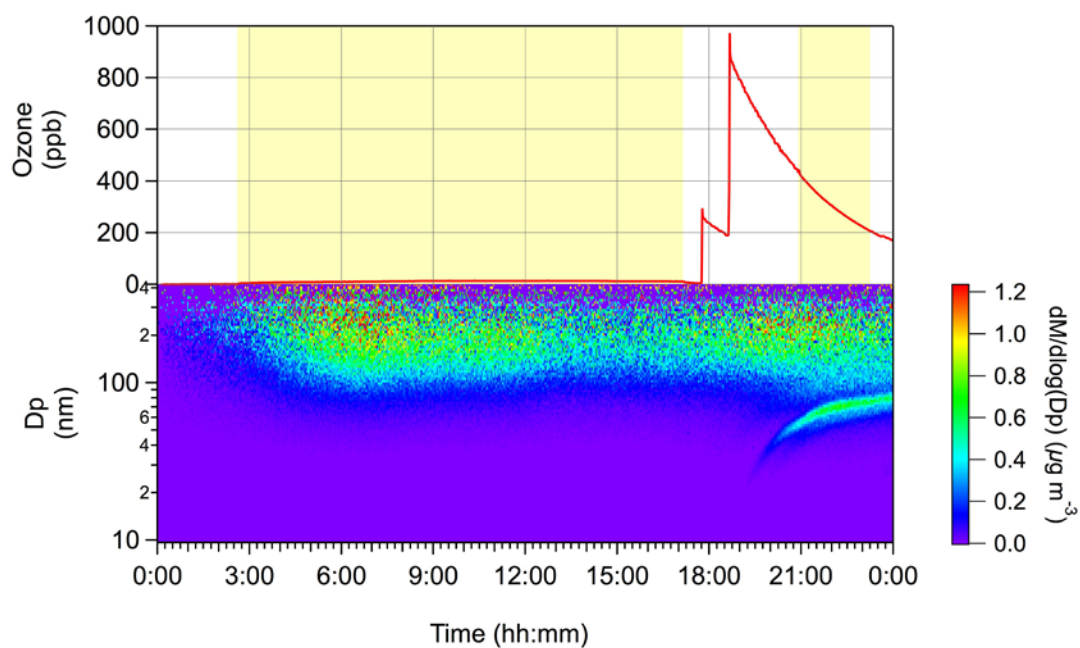
Figure S4. Time series of particle mass size distributions in the multiphase simulation chamber an experiment in the presence of nonanoic acid and humic acid (NA = 0.1 mM; HA = 10 mg L^{-1}). The red line represents the ozone concentration. The yellow part represents the period when the lights were on (Exp. 2 in Table 1).

References

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