Supporting information for

New insights into the nonlinear effects of NO_x-isoprene photo-oxidation

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Text-S1 Vapor wall loss corrections for SOA yield

Our study also corrected loss of vapors to the chamber wall by the first-order wall-loss coefficient kw (s^{-1}) by Zhang et al. (2014). The value of k_w use the gas-phase transport parameters within a chamber. Mcmurry and Grosjean (1985) present a formula for k_w.

$$k_w = \left(\frac{A}{V}\right)\frac{\left(\frac{\alpha_w \bar{c}}{4}\right)}{1.0+\left(\frac{\pi}{2}\right)\left[\frac{\alpha_w \bar{c}}{4\left(k_e D_{gas}\right)^{0.5}}\right]} \quad (1)$$

where A/V is the surface to volume ratio of the chamber (the ratio was 4 m^{-1} in this study), α_w is the mass accommodation coefficient of vapors onto the chamber walls, and 10^{-5} was adopted according to the experimental results of Matsunaga and Ziemann (2010), $\bar{c}$ is the mean thermal speed of the molecules. k_e is the coefficient of eddy diffusion, and 0.12 $s^{-1}$was estimated according to the values reported by previous studies for a 4 m^3 Caltech chamber (Mcmurry and Grosjean, 1985). D_{gas} is the molecular diffusivity. For the type of molecules here, D_{gas} is ~1.38 10^{-5} m^2 s^{-1} and $\bar{c}$~ 299 m s^{-1}. For a given vapor molecule, the mean thermal speed $\bar{c}$ could be calculated according to the following equation:

$$\bar{c} = \sqrt{\frac{8\mathrm{RT}}{\pi \mathrm{MW}}} \quad (2)$$

in which R is the ideal gas constant (i.e., 8.314 J mol^{-1} K^{-1}), T is the experimental temperature (T=288.15 K in this study), and MW is the molecular weight.

Text-S2 The saturation vapor pressure (C*)

Based on the method developed by Li et al. (2016) to estimate saturated vapor pressure (C^*) through molecular formulas, this study estimates the C^* of the main gas phase HOMs products in the photooxidation process of isoprene under the influence of NO_x:

$$logC^* = (n_c^0 - n_c)b_c - n_0 b_0 - 2\frac{n_c n_0}{n_c + n_0}b_{co} - n_N b_N - n_s b_s$$

where n_c^0 is the number of reference carbon atoms, n_c, n_0, n_N, n_s are the number of carbon, oxygen, nitrogen, and sulfur atoms, respectively; b_c, b_0, b_N, b_s are the contribution of each atom to $logC^*$, respectively, and bco is the carbon-oxygen non-inertness factor.

Text-S3 NO_3 calculation

The NO_3 concentration were calculated to analyze the role of NO_3 in SOA formation. The calculation methods are as follows:

$$NO_2 + O_3 \xrightarrow{k_1} NO_3 + O_2 \quad (3)$$

$$NO_3 + Isoprene \xrightarrow{k_2} products \quad (4)$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2 \quad (5)$$

$$NO_2 + NO_3 + M \xrightarrow{k_4} N_2O_5 + M \quad (6)$$

$$N_2O_5 + M \xrightarrow{k_5} NO_2 + NO_3 + M \quad (7)$$

$$N_2O_5 + H_2O(s) \xrightarrow{k_{N_2O_5}} 2HNO_3 \quad (8)$$

Once the NO_3 radical is produced via R3, it rapidly establishes thermal equilibrium with N_2O_5 in the presence of NO_2 (reactions (6) and (7)), which can be summarized as:

$$[N_2O_5] = k_{eq}[NO_2][NO_3],\ k_{eq} = k_4/k_5 \quad (9)$$

k_{eq} is calculated by the method given by Yan et al., (2023). Assuming that NO_3 and N_2O_5 are in a steady-state condition, their total formation rate is roughly the same as the total loss rate, and much greater than the net change rate, then the steady-state NO_3 mixing ratios are expressed by Eq. (10)

$$[NO_3]ss = \frac{k_1[NO2][O3]}{k_2[Isop]+K_3[NO]+J_{NO_3}+k_{N_2O_5}k_{eq}[NO_2]} \quad (10)$$

With a room temperature, rate constant of k_1= 3.2 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1}; k_2 = 6.5 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}; k_3=2.6 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}; J_{NO_3} is the sum of the photolysis coefficients of the two photolysis reactions of NO_3, 0.176 s^{-1}(Brown and Stutz, 2012). The $k_{N_2O_5}$ is the heterogeneous uptake rate of N_2O_5 on the aerosol surface, which can be calculated by Eq. (11):

$$k_{N_2O_5} = \frac{1}{4}cS\gamma \quad (11)$$

Where C is the mean molecular speed of N_2O_5, which is 240 m s^{-1}, S is the concentration of total particle surface area, which can be calculated based on the particle number size distribution, and γ is the uptake coefficient of N_2O_5 (Hu et al., 2023).

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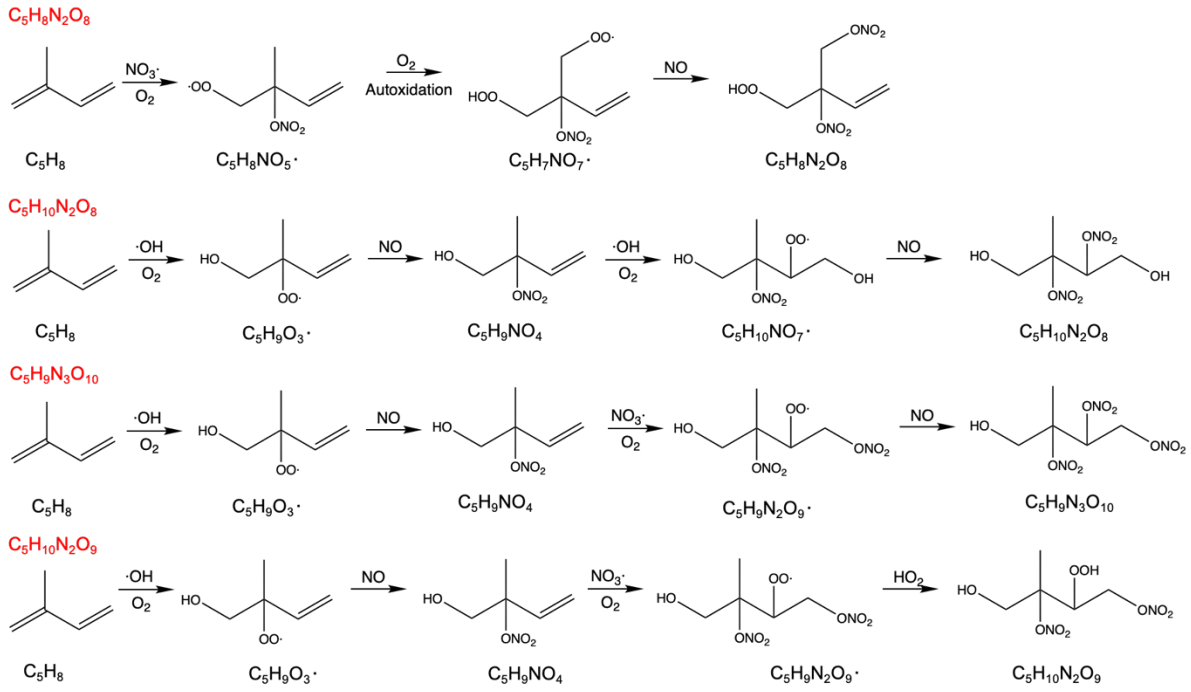

Figure S1. Simplified formation mechanism of $C_5H_8N_2O_8$, $C_5H_{10}N_2O_8$, $C_5H_9N_3O_{10}$ and $C_5H_{10}N_2O_9$.

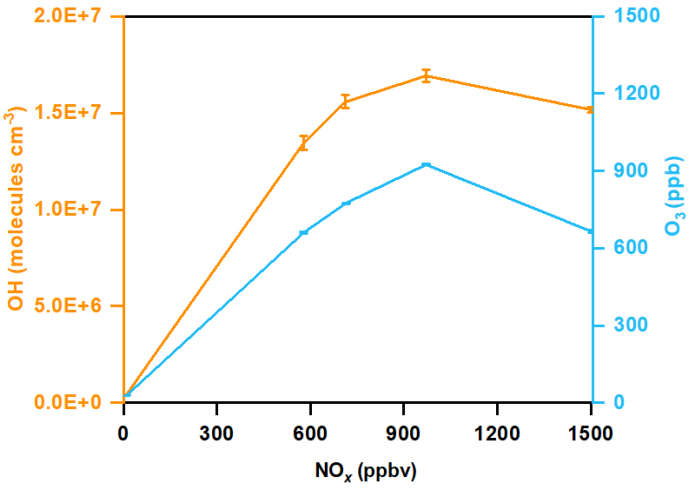

Figure S2. Variations of OH and O_3 concentrations.

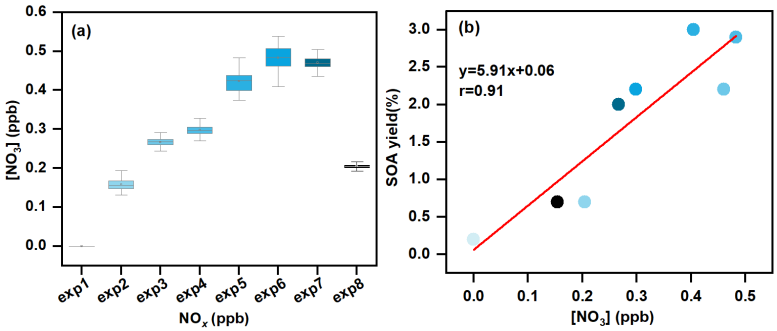

Figure S3. (a) calculated concentrations of NO_3 radicals in the varying NO/NO_2 experiments; (b) correlation between NO_3 and SOA yield.

Table S1. The $\log_{10}C^*$ of low volatile organic products

Molecular formula	$\log_{10}C^*$	VOC type[a]
$C_5H_8N_2O_8$	-0.92	LVOC
$C_5H_{10}N_2O_8$	-0.92	LVOC
$C_5H_8N_2O_9$	-1.67	LVOC
$C_5H_{10}N_2O_9$	-1.67	LVOC
$C_5H_9N_3O_{10}$	-3.54	LVOC
$C_5H_9N_3O_{11}$	-4.30	LVOC
$C_5H_{11}N_3O_{11}$	-4.30	LVOC
$C_5H_9N_3O_{12}$	-5.06	LVOC
$C_6H_{10}N_2O_{14}$	-5.75	ELVOC
$C_{10}H_{17}N_3O_{14}$	-8.08	ELVOC
$C_{10}H_{17}N_3O_{16}$	-9.57	ULVOC
$C_{12}H_{20}NO_{17}$	-8.71	ULVOC
$C_{15}H_{20}N_2O_{14}$	-8.75	ULVOC
$C_{15}H_{17}N_2O_{17}$	-10.78	ULVOC

[a]VOC type is defined according to the following ranges: ultralow volatility organic compounds (ULVOCs, $\log_{10} C^* < -8.5$,), extremely low volatility organic compounds (ELVOCs, $-8.5 < \log_{10} C^* < -4.5$), low volatility organic compounds (LVOCs, $-4.5 < \log_{10} C^* < -0.5$), semivolatile organic compounds (SVOC, $-0.5 < \log_{10} C^* < 2.5$), intermediate volatility organic compounds (IVOC, $2.5 < \log_{10} C^* < 6.5$), and volatile organic compounds (VOC, $\log_{10} C^* > 6.5$).(Li et al., 2016)