Supporting Information for

Gas-phase kinetics modifies the CCN activity of biogenic SOA

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Contents of this file: Derivation of reaction kinetics, CCN calibration data, CCN charge correction example and alternate gas-phase analysis.

Introduction: The derivation of equations used in the text are provide on Page 1. The $(NH_4)_2SO_4$ calibration for CCN instrumentation is available on page 2.

Derivation of kinetics for nth order analysis:

Each 90 m^3 environmental reaction chamber can be modeled as an ideal batch reactor. Where, at time, $t = 0$, there is no flow in and out of a well-mixed system. The initial concentration of the measured reactant (A), C_{ao} and the concentration of reactant A at any time is, C_a. The overall reaction rate can be expressed as the product of the overall reaction rate constant, k and C_a^n; where n, is the pseudo-order of the overall reaction. Ca may refer to a singular precursor reactant or the summation of reactants in the system. The equation for the concentration of the reactant, C_a, at any given time are derived below.

A. For n = 1 order reactions:

The design equation for a batch system is as follows:

$$\frac{dC_a}{dt} = k{C_a}^n, where\ n = 1$$

$$\int k\ dt = \int \frac{dC_a}{C_a}$$

$$kt = \ln C_a \,\Big|_{C_{a0}}^{C_a}$$

$$kt = \ln C_A - C_{ao}$$

B. For n ≠ 1, the integrated design equation is:

$$\int k\ dt = \int \frac{dC_a}{{C_a}^n}$$

$$kt = \frac{\left(\frac{C_A}{C_{A0}}\right)^{n-1} - 1}{n-1}$$

$$\frac{kt}{{C_A}^{1-n}}$$

CCN Counter Calibration Data

Table SI1. CCNC Calibration Data

Calibration applied to SOA Experiment	SS % Setting	Dp_{50} [µm]	Calibrated SS %
Isoprene + OH	0.2	0.073	0.24
Isoprene + OH	0.2	0.073	0.24
Longifolene + OH	0.2	0.073	0.24
Longifolene + OH	0.2	0.074	0.23
Isoprene + Longifolene + OH	0.2	0.073	0.24
Isoprene +	0.2	0.073	0.24

Longifolene + OH

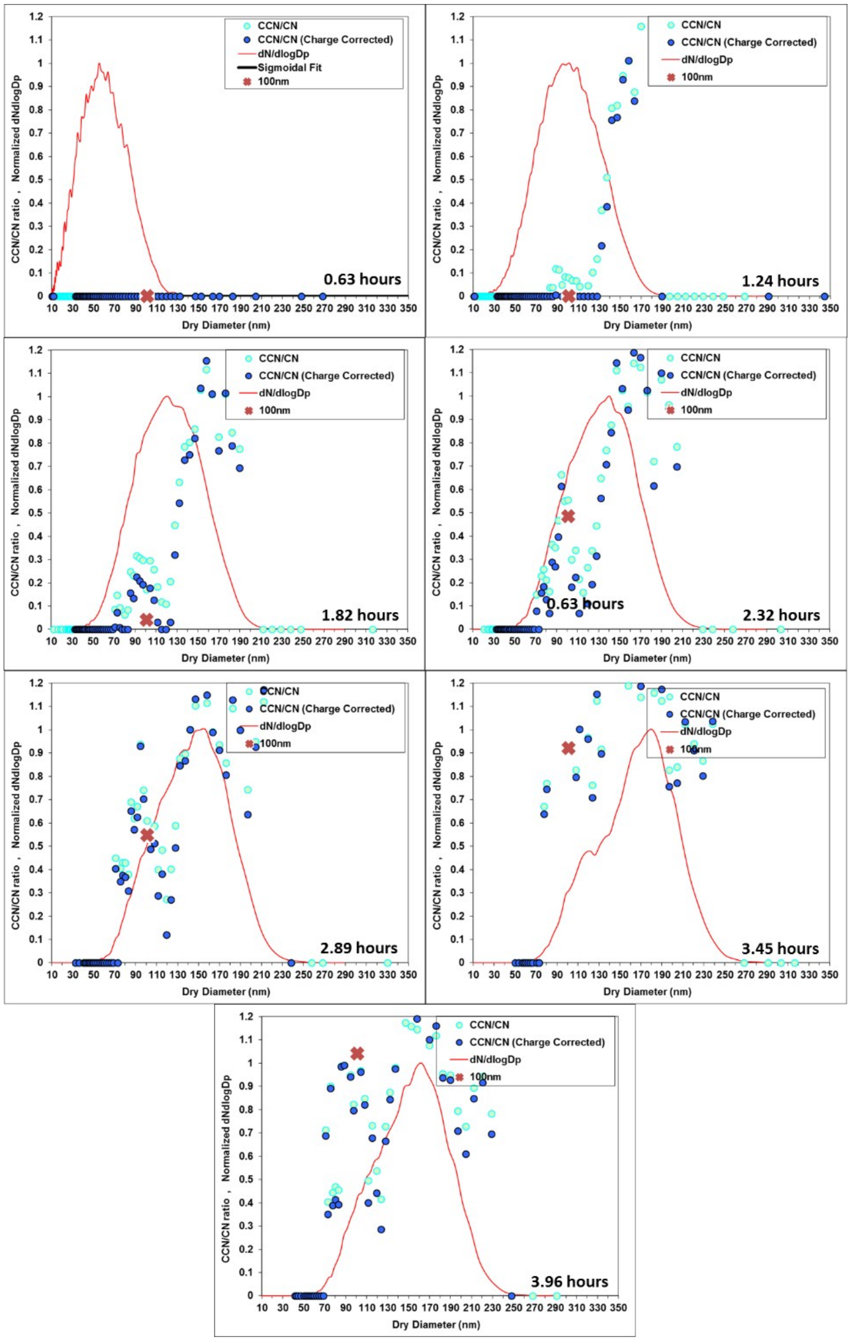

Figure SI1. Charge corrected sigmoids for a longifolene experiment. 100 nm charge corrected particles are marked with a red X.

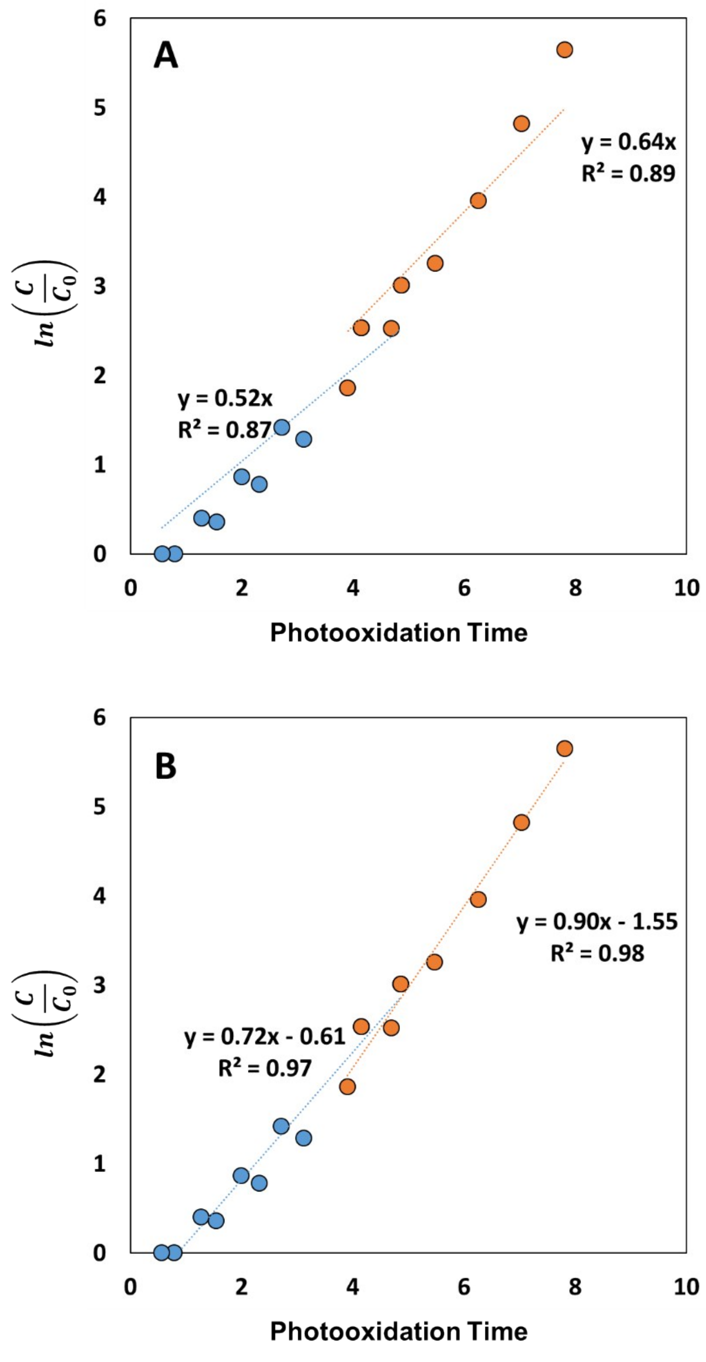

Figure SI2. Mixture gas-phase kinetics assuming 2 first-order decays. A.) Fits forced through 0. B.) Fits not forced through 0.

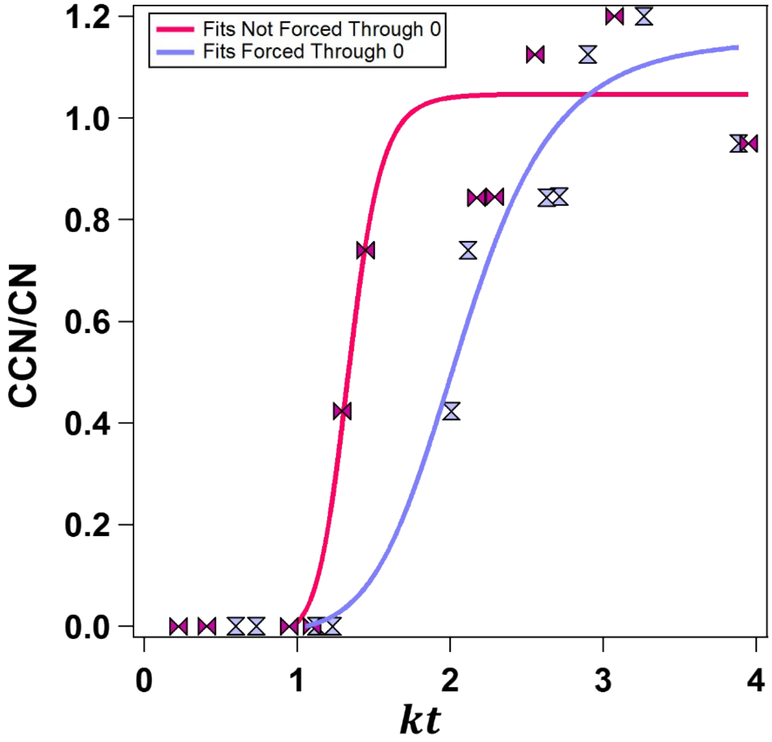

Figure SI3. Alternate sigmoids using gas-phase fits of Figure SI2.

	Forced Through 0		Not Forced Through 0	
	k_1'	k_2'	k_3'	k_4'
1st order k'	0.52	0.64	0.72	0.90
t_{50gas}'	4.02	3.26	1.87	1.48

Table SI2. Summary of alternate fit results. 1st order k' and predicted t_{50gas} values are identified.

Discussion of Alternative Kinetics

Here, we attempted to recreate the gas-phase CCN sigmoids using alternative kinetics for the mixture system by assuming 2 first-order reactions were occurring in the systems: once before the critical time and one after. These fits (Figure SI2) were then used to find the critical gas-phase CCN times and are summarized in Table SI2. These alternative analyses do not accurately predict the critical times for the mixture system. The only fit that comes close is that of the k2’ prediction from the gas-phase analysis that is forced through 0. This analysis shows that we must use pseudo-nth order kinetics to accurately predict the critical times of the mixture systems.