Supporting Information of

Dithiothreitol Activity by Particulate Oxidizers of SOA Produced from Photooxidation of Hydrocarbons under Varied NO$_x$ Levels

Section S1. Outdoor chamber experiments.

5 A non-reactive compound, CCl$_4$ (500-1000 ppb), was injected into the chamber as a dilution tracer. Gas phase concentrations of hydrocarbons and CCl$_4$ were measured by a gas chromatography-flame ionization detector (GC-FID, HP-5890). The concentration of NO$_x$ was monitored by a chemiluminescence analyzer (Teledyne, Model T201). The concentration of O$_3$ was monitored by a photometric ozone analyzer (Teledyne, Model 400E). The relative humidity

10 and temperature were monitored by a hygrometer (CS215-L, Campbell Scientific).

Section S2. Chemicals and solution preparation.

Toluene (99.5 %), 1,3,5-trimethylbenzene (99 %), and hydrogen peroxide (50 wt.% aqueous solution) were from Acros Organics (NJ, USA). Isoprene (99 %), α-pinene (98 %), CCl$_4$ (99.9 %), potassium phosphate buffer (0.1 M), 9,10-phenanthraquinone (99 %), 1,4-naphthoquinone

15 (97 %), mesityl oxide (90 %), 2,4-hexadienal (>95 %), sulfanilic acid (99 %), n-(1-naphthyl) ethylenediamine dihydrochloride (≥98 %), potassium hydroxide (≥85 %), sodium nitrite (≥97 %), tert-butyl hydroperoxides (5.0-6.0 M in decane), peracetic acid (32 wt.%), tert-butyl peroxide (98 %), dimethyl sulfoxide (99.9 %) and 4-nitrophenyl boronic acid (≥95 %) were from Sigma-Aldrich (St. Louis, MO, USA). Dithiothreitol (99 %), Tris base (99.8-100.1 %), 5,5'-

20 dithiobis-(2-nitrobenzoic acid) (99 %), trichloroacetic acid (99 %), and deionized (DI) water (ACS, ASTM Type I) were obtained from Thermo Fisher Scientific (Pittsburgh, PA, USA). Acrolein (97 %, stabilized by hydroquinone) was from Alfa Aesar (Ward Hill, MA, USA).

The preparation details of 9,10-phenanthraquinone (PQN), 1,4-naphthoquinone (NQN), tert-butyl peroxides, and tert-butyl hydroperoxides were shown below:

25 **PQN stock solution:** 5 mM PQN standard stock solution was made by dissolving 20.821 mg of PQN in 20 mL DMSO. The stock solution was kept at 4 °C when not in use. Before chemical analysis, the PQN stock solution was diluted using DI water.

NQN standard: 5 mM NQN standard stock solution was made by dissolving 31.630 mg of NQN in 20 mL DMSO. The stock solution was kept at 4 °C when not in use. Before chemical analysis, the NQN stock solution was diluted using DI water.

Tert-butyl peroxide: 26 mM tert-butyl peroxide solution was prepared by adding 0.1 mL tert-butyl peroxide (98 %) into 20 mL DI water. The tert-butyl peroxides stock solution was further diluted to get a 100 µM using DI water.

Tert-butyl hydroperoxides: 22 mM tert-butyl hydroperoxide solution was prepared by adding 0.08 mL tert-butyl hydroperoxide (5.0-6.0 M in decane) into 19.92 mL methanol. The tert-butyl hydroperoxides stock solution was further diluted to get a 96 µM using methanol.

Section S3. The limit of detection of chemical assays.

The limit of detection of each chemical assay is defined as three times the standard deviation (σ) of blank controls, shown in Table S1.

Table S1. Limit of detection of chemical assays

Chemical assay	Dithiothreitol (DTT) measurement	Griess assay	NPBA assay
Limit of detection	0.23 nmol/min	0.60 µM	0.47 µM

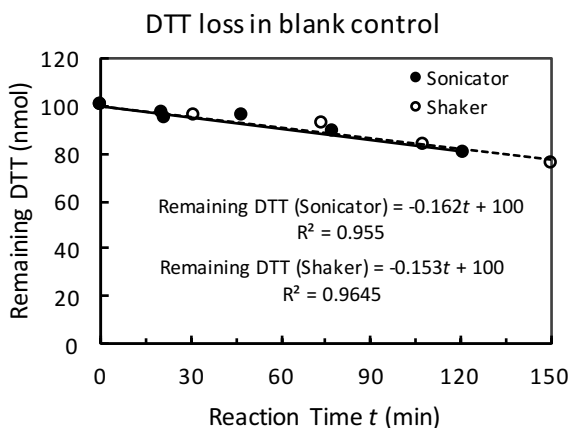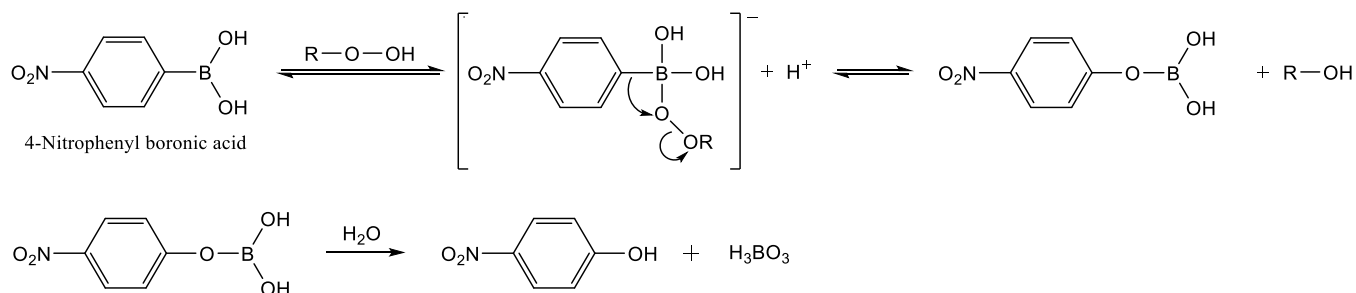**Section S4. The blank control of DTT assay**

Figure S1. DTT loss in blank control (deionized water) during sonication or shaking (37 °C).

Section S5. Schemes of 4-nitrophenylboronic acid (NPBA) assay and quantification of organic hydroperoxides in secondary organic aerosols (SOA) using NPBA assay.

Scheme S1. Scheme of the reaction between 4-nitrophenylboronic acid (NPBA) and organic hydroperoxides (Kuivila, 1954; Kuivila and Armour, 1957).
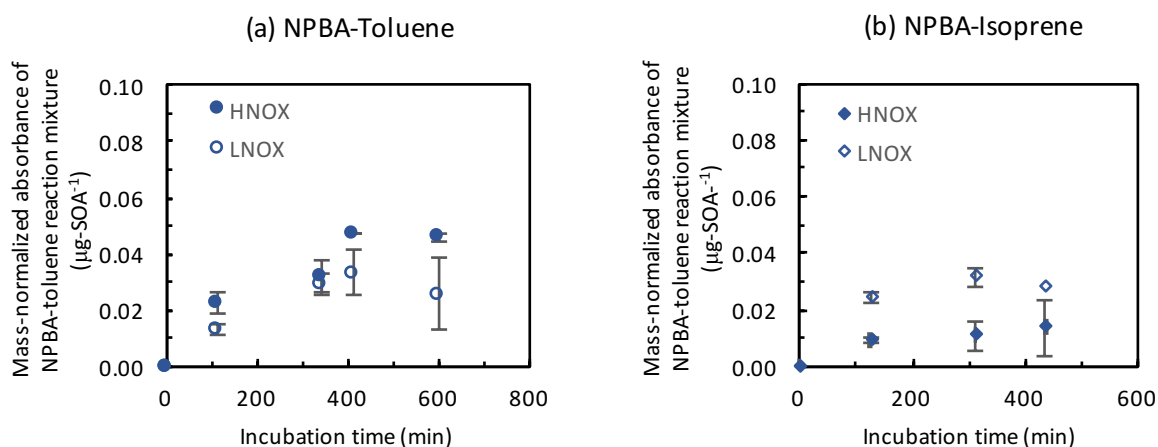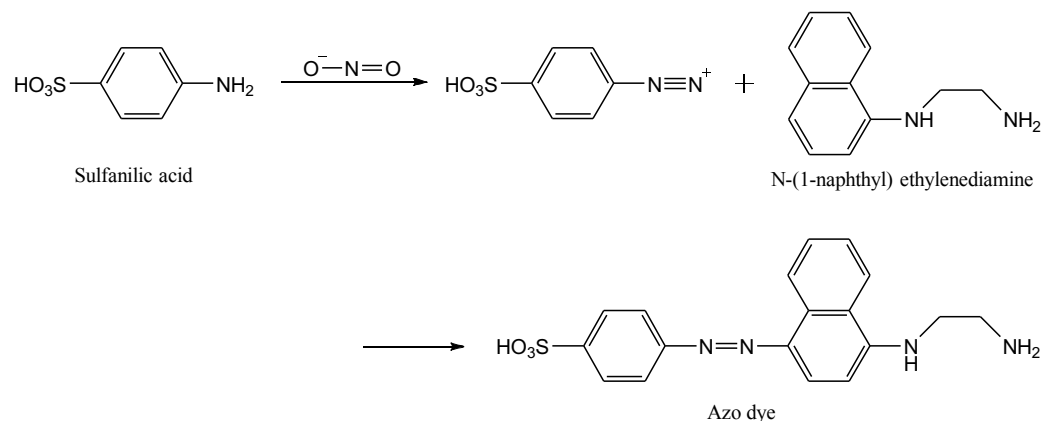

Figure S2. Time profile of the absorbance (normalized by SOA mass) of NPBA-SOA reaction mixture at 85 °C. The error bar of each data point represents the standard deviation of three replicates.

Section S6. Scheme of Griess assay.

Scheme S2. Scheme of the reaction between Griess reagent (sulfanilic acid and n-(1-naphthyl) ethylenediamine) and nitrites (Giustarini et al., 2008).

Section S7. Lifetime of electron-deficient alkenes under typical chamber conditions.

Electron-deficient alkenes produced from the photooxidation of hydrocarbons can further react with oxidants, such as OH radicals and O_3 (Finlayson-Pitts and Pitts Jr, 2000). The lifetime (τ) of acrolein, a representative electron-deficient alkene, was estimated using (Finlayson-Pitts and Pitts Jr, 2000):

$$\tau = \frac{1}{k[\text{oxidant}]} \tag{1}$$

where [oxidant] is the concentration of atmospheric oxidants (i.e., O_3 and OH radicals), and k is the rate constant for the reaction of acrolein with atmospheric oxidants ($k_{OH} = 2\times10^{-11}$ cm^{-3} molecule^{-1} s^{-1} and $k_{O_3} = 2.9\times10^{-19}$ cm^{-3} molecule^{-1} s^{-1}) (Saunders et al., 2003, 1997). The typical concentration of OH radicals during the photooxidation of toluene under low NO_x conditions was about 2×10^{-4} ppb at 13:00, estimated using the Master Chemical Mechanism (Saunders et al., 2003, 1997). The typical concentration of ozone was about 200 ppb at 13:00. Then, the lifetime of acrolein is 208 h in the presence of ozone and 3 h in the presence of OH radicals.
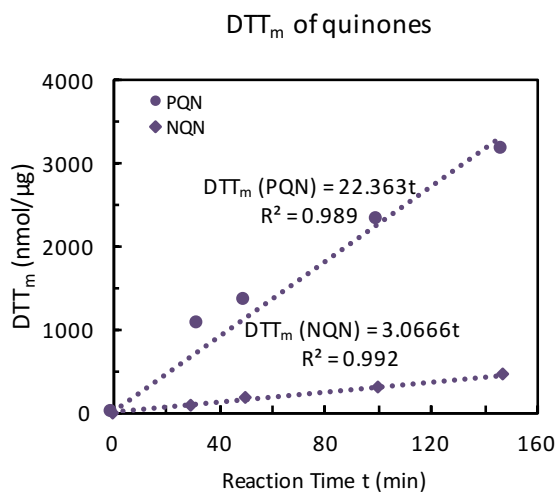
Section S8. Other supporting figures

DTT$_m$ of quinones

Figure S3. Time profile of DTT$_m$ of quinones (PQN: 9,10-phenathraquinone, NQN: 1,4-naphthoquinone).

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(a) Particle phase PAN (Isoprene)
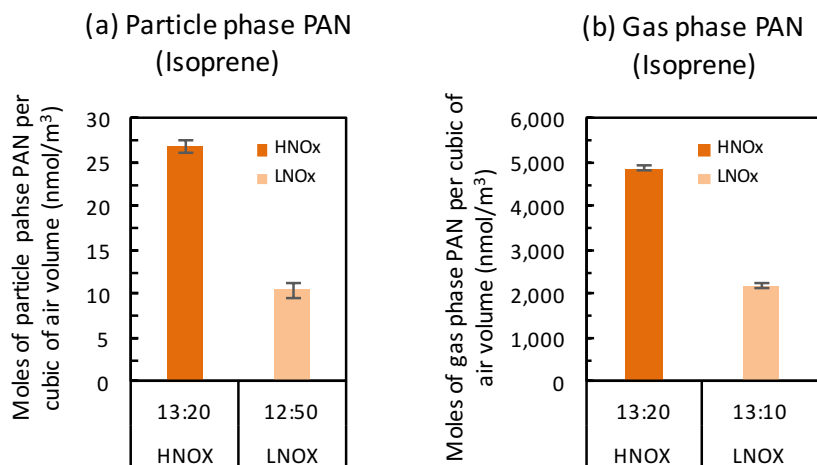
(b) Gas phase PAN (Isoprene)

Figure S4. For isoprene experiment (22 Jul. 2016), the concentrations of gas and particle phase PAN products were measured (HNOX: high NO_x conditions, LNOX: low NO_x conditions). (a) The moles of particle phase PANs (collected by a particle-into-liquid sampler) per cubic of air volume. (b) The moles of gas phase PANs (collected by an impinger) per cubic of air volume. The error bar of each column is the standard deviation of three replicates. The collection efficiency of the impinger was not determined in this study. However, the concentration of gaseous PAN products was at least 200 times higher than that of particulate PAN products as shown in Figure above. The x-axis represents the mid-collection time (Table 1).
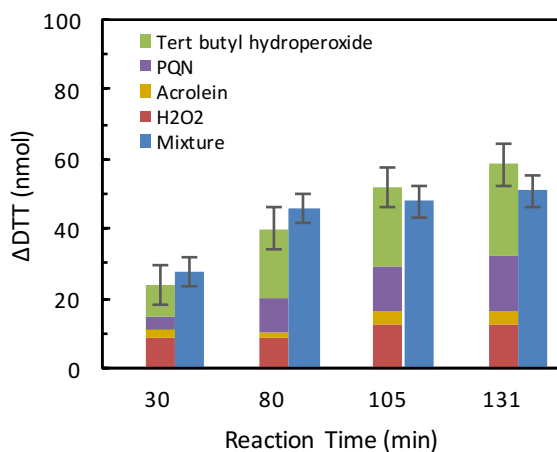
ΔDTT of a mixture of model compounds

Figure S5. The DTT consumption (ΔDTT) by individual model compounds and the mixture of model compounds (54 nmol acrolein, 15 nmol H_2O_2, 280 nmol tert-butyl hydroperoxides, 0.025 nmol PQN). The error bar associated with ΔDTT of a stacked column was estimated by the sum of the error bars from individuals.

Reference:

Finlayson-Pitts, B. J. and Pitts Jr, J. N.: Chapter 6 - Rates and mechanisms of gas-phase reactions in irradiated organic−NO$_x$−air mixtures. In: Chemistry of the Upper and Lower Atmosphere, Pitts, B. J. F.-P. N. (Ed.), Academic Press, San Diego, 2000.

Giustarini, D., Rossi, R., Milzani, A., and Dalle-Donne, I.: Nitrite and nitrate measurement by Griess reagent in human plasma: evaluation of interferences and standardization, Method. Enzymol., 440, 361-380, 2008.

Kuivila, H. G.: Electrophilic displacement reactions. III. kinetics of the reaction between hydrogen peroxide and benzeneboronic acid[1], J. Am. Chem. Soc., 76, 870-874, 1954.

Kuivila, H. G. and Armour, A. G.: Electrophilic displacement reactions. IX. effects of substituents on rates of reactions between hydrogen peroxide and benzeneboronic acid[1-3], J. Am. Chem. Soc., 79, 5659-5662, 1957.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-180, 2003.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: World wide web site of a master chemical mechanism (MCM) for use in tropospheric chemistry models, Atmos. Environ., 31, 1249, 1997.