SUPPORTING INFORMATION

The Photochemical Conversion of Surrogate Emissions for Use in Toxicological Studies: Role of Particulate- and Gas-Phase Products

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Table S1. The 20 Major Hydrocarbons and Their Average Initial Concentrations and Percent Composition in the Initial Chamber Mixture[a]

SA-PM			SA-O_3		
Compound	Ave. Conc. (ppbC)	Comp (%)	Compound	Ave. Conc. (ppbC)	Comp (%)
α-Pinene	5400	18.9	Isoprene	5275	40.0
Toluene	3349	11.7	Toluene	1135	8.6
Ethanol	2170	7.6	2-Methylpentane	663	5.0
2-Methylpentane	2016	7.1	Ethanol	650	4.9
m&p-Xylene[b]	1727	6.1	m&p-Xylene[b]	641	4.9
n-Hexane	1363	4.8	n-Hexane	437	3.3
3-Methylpentane	1148	4.0	3-Methylpentane	367	2.8
Isopentane	1106	3.9	Isopentane	341	2.6
n-Pentane	532	1.9	1,2,4-TMB	202	1.5
Methylcyclopentane	515	1.8	Ethylbenzene	175	1.3
1,2,4-TMB	509	1.8	Methylcyclopentane	167	1.3
Ethylbenzene	481	1.7	n-Pentane	166	1.3
Cyclohexane	410	1.4	o-Xylene	153	1.2
2,3-Dimethylbutane	354	1.2	Cyclohexane	135	1.0
m-Ethyltoluene	321	1.1	m-Ethyltoluene	123	0.9
2-Methyl-2-butene	321	1.1	2,3-Dimethylbutane	112	0.9
n-Butane	320	1.1	2-Methyl-2-butene	97	0.7
o-Xylene	293	1.0	n-Butane	96	0.7
trans-2-Pentene	266	0.9	trans-2-Pentene	89	0.7
2-Methylhexane	231	0.8	1,3,5-TMB	85	0.6
Others	5704	20.0	Others	2091	15.8

[a]Although the order was not identical in each experiment, the table accurately depicts the typical ordering.

[b]m-Xylene and p-Xylene co-elude and are reported as a single concentration.

Table S2. Average Carbonyl Concentrations in the Chamber (ppbv) during Irradiations for Selected Experiments[a]

Carbonyl Compound	SA-PM		SA-O_3	
	MR052	MR055	MR059	MR062
Formaldehyde	256	228	502	581
Acetaldehyde	242	217	79	86
Acrolein	13	4.2	ND[b]	ND[b]
Acetone	138	128	40	35
Propionaldehyde	66	65	33	36
Methacrolein	0.8	3.4	66	84
Butyraldehyde	27	29	ND[b]	9.0
2-Butanone	32	27	12	9.5
Benzaldehyde	2	3.2	ND[b]	3.3
Glyoxal	23	28	34	50
m-Tolualdehyde	ND[b]	1.4	ND[b]	ND[b]
Valeraldehyde	5.7	6.8	ND[b]	ND[b]
Methyl Glyoxal	60	69	126	143

[a]Although carbonyl measurements prior to MR052 were unavailable, reported concentrations for MR052 and MR055 were representative of expected concentrations in all SA-PM studies.

[b]Not detected.

Wall loss correction of particle phase Organic Mass (OM) and Organic Carbon (OC)

Diffusion of particle bound organic mass and organic carbon to the walls of the MRC chamber during photochemical processing was corrected for in calculations of yields.

$$[OC]_{corrected} = [OC]_{raw}\, e^{k_{diffusion}t}$$

Where t is photochemical residence time of the MRC (in this case 4 hours) and $k_{diffusion}$ is the particle phase diffusion loss rate determined experimentally. Fresh injections of reactants were stopped and the decay of PM concentrations were observed over a number of experiments to determine a total loss rate (k). The loss due to diffusion ($k_{diffusion}$) was determined empirically by

$$k_{diffusion} = k - k_{dilution}$$

$k_{diffusion}$ was found to average 0.0835 hr^{-1} across all experiments tested.

Secondary organic aerosol/carbon yield calculation

The SOA yield (γ_{SOA}) was calculated by

$$\gamma_{SOA} = \frac{\Delta[OM]}{\Delta HC}$$

Where $\Delta[OM]$ (µg m^{-3}) is the amount of organic mass formed through photochemistry and ΔHC (µg m^{-3}) is the amount of parent hydrocarbon reacted during the experiment. The SOC yield (γ_{SOC}) was calculated by

$$\gamma_{SOC} = \frac{\Delta[OC]}{\Delta HC}$$

Where $\Delta[OC]$ (µgC m^{-3}) is the amount of organic carbon in the particulate phase formed through photochemistry and ΔHC (µgC m^{-3}) is the amount of parent hydrocarbon carbon reacted during the experiment.

Hydrocarbon Analysis by GC-FID

The VOCs were determined using GC-FID procedures. Chamber samples were injected onto the GC column using a 2 stage pre-concentration procedure to remove the VOCs from the sample air prior to injection. The GC column used consisted of a 60-m x 0.32-mm I.D. fused silica column having a 1-μm DB-1 coating (J&W Scientific). Helium was used as the carrier gas with column flow controlled with an electronic pressure control (EPC) system maintained at constant pressure. The column temperature was initially set to -50˚C for 2 min, followed by a temperature ramp from -50˚C to 200˚C at a rate of 8˚C min-1, followed by a temperature hold for 7.75 min. A second temperature ramp to 225˚C with a hold time of 13min ensured the elution of higher MW compounds. The eluting peaks were identified by column retention time using a calibration table (CALTABLE) containing more than 300 compounds. To confirm the identity of specific compounds observed in the sample air, as well as, to provide identification of unknown compound peaks, a Hewlett-Packard 5972 GC-MS with a similar GC column and He flow conditions was used.

Chamber Sampling

Samples were collected from the chamber and inlet systems using a 3-L Teflon bag, which was taken to the analytical laboratory for detailed GC analyses for both the VOC precursors and photo-oxidation product peaks. At times, the bag samples were transferred to 6-L surface-conditioned canisters and stored for later GC analysis of the VOCs.

GC Systems

Samples taken from the chamber were analyzed using gas chromatography combined with flame ionization detection (GC/FID, Hewlett-Packard Model 5890). The column used

consisted of a 60 m x 0.32 mm ID fused column containing a 1-µm DB-1 coating (J&W Scientific). Column operation consisted of a -50°C initial temperature for held for 2 min followed by temperature programming to 200°C at a rate of 8°C min^{-1}. After a 7.75-min hold period, column temperature was programmed to 225°C at a 25°C min^{-1} rate and held at that temperature for 8 min. Liquid nitrogen was used as the cryogen to obtain the sub-ambient temperatures required in this programming sequence. The column helium carrier gas flow was maintained at 150 kPa using an electronic pressure control (EPC) device. The eluting compound peaks were identified by column retention time location using a calibration table that contain more than 300 compounds. Compound peak identification was verified using a similar GC column system equipped with a mass spectra detection system (GC/MS). All GC column temperature programming conditions were identical, however, the (EPC) device was set with a constant carrier gas flow of 1.4 ml min^{-1}.

Peroxyacetyl nitrate (PAN) was also observed in the chamber as a product of the photo-oxidation process, and compound concentrations were determined using a gas chromatographic electron capture detector (GC/ECD) approach. The detector system consisted of a pulse discharge Model D-2 (Valco Instrument Co., Houston, TX) device configured to operate in the electron capture mode (abbreviated as PDECD). The GC column used was a 30 m x 0.53 mm ID fused silica column coated with a 1.0-µm Rtx-200MS liquid phase maintained at 25°C (Cat.# 15655-6850, Restek, Bellefonte, PA). Detector gas flows were adjusted for proper operation of the PDECD: helium at 30 cm^3 min^{-1} through the pulsed DC discharge to produce ionization source, and a 3 cm^3 min^{-1} of a 5% CH_4 in helium dopant gas to create a detector standing current, and a GC column carrier gas flowrate of 11.5 cm^3 min^{-1}. The detector temperature was controlled at 60°C.

Carbonyl Analysis

Sample Collection

A 4-mL volume of acidified 2,4-dinitrophenylhydrazine (DNPH) solution was pipetted to a 24/40 size glass impinger for the sample collection. The impinger was transferred to the mobile chamber facility and immersed in an insulated ice bath during the sampling period. The impinger was connected inline between the sample chamber and a Singer, American Meter Division Model 802 pump for flow and volume measurement. Flow was calibrated at 0.5 L min^{-1} and samples collected for 20 min for a total nominal volume of 10 L.

Following the collection period, the final sample volumes were measured and transferred to clear glass vials with teflon-lined screw caps and stored -20^{o}C. For all investigations, 2,4-DNPH blanks were taken at the beginning of the study, the beginning and end of each week, and at the end of the study. Just before analysis, all blanks and samples were heated at 70°C for 30 min to drive the DNPH derivatization to completion.

Chemical Materials

A 15 component standard mixture of 2,4-dinitrophenylhydrazone aldehyde and ketone derivatives was used for the instrument calibration and chamber sample analysis. The derivatives include: formaldehyde-DNPH, acetaldehyde-DNPH, acrolein-DNPH, acetone-DNPH, propionaldehyde-DNPH, crotonaldehyde-DNPH, methacrolein-DNPH, butyraldehyde-DNPH, 2-butanone-DNPH, benzaldehyde-DNPH, glyoxal-DNPH, valeraldehyde-DNPH, m-tolualdehyde-DNPH, methyl glyoxal-DNPH, and hexaldehyde-DNPH.

The Supelco *Carb Method 1004 DNPH Mix 2* (Part# 47651-U) hydrazone standard (30

μg mL^{-1} - free carbonyl) and a separate hydrazone standard of glyoxal-DNPH and methyl glyoxal-DNPH were used to prepare a three-level calibration standard solution set. A separate hydrazone standard acquired from AccuStandard, Inc., Carbonyl Compounds as DNPH Derivatives (Part# M-1004) at 3 μg mL^{-1} (free carbonyl) was used for quality control purposes. Fisher Scientific HPLC-grade acetontrile, methanol, and water were used for the analysis and chemical preparations.

Instrumentation

The samples were analyzed using a Hewlett-Packard (HP) 1100 HPLC system equipped with solvent degasser, quaternary pump, autosampler, thermostat controlled column compartment, and diode array detector (DAD). HPLC system control and data processing were managed using a HP data station with ChemStation chromatography software. A ternary gradient consisting of acetonitrile, methanol, and water was used to conduct the chromatographic analysis. SI Table 1 shows the gradient and flow rate schedule.

Table S3. HPLC Gradient-Flow Schedule for DNPH-Carbonyl Analysis

Time (min)	Acetonitrile (%)	Methanol (%)	Water (%)	Flow (mL min^{-1})
0	20	40	40	1.0
20	5	70	25	1.0
30	5	80	15	1.0
40	5	80	15	1.0

A 10 μL injection volume was used for all standards and samples and an Agilent Zorbax ODS 4.6 x 250 mm, 5 μ particle column, maintained at 40°C, for the chromatographic separation. The diode array (UV) detector was set to a 360 nm wavelength (ʎ) and 10 nm

bandwidth for signal detection.

Calibration and Quality Control

Four studies were conducted: MR055, MR059, MR060, and MR062. The three-point calibration curves generated for each study produced, at a minimum, correlation coefficients of at least 0.999 for all carbonyl species. Calibration standard checks and an independent quality control solution analysis were also performed with a difference of ≤ 4% and ≤ 10% observed, respectively, compared to the prepared carbonyl concentrations (QC analysis excluded glyoxal and methyl glyoxal due to unavailability).

Sample Analysis

Sample concentrations were initially calculated in units of nanomole per mL (nmole/mL) and then converted to ppbv based on the final DNPH sample volume in milliliters (mL), chamber volume sampled in liters (L), and the molar volume of air in liters (L) at normal temperature and pressure (NTP). Sample results (blank subtracted) follow for each study.