

Ozone-Initiated Reactions with Mixtures of Volatile Organic Compounds under Simulated Indoor Conditions

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This study examines the primary and secondary products resulting from reactions initiated by adding ozone to complex mixtures of volatile organic compounds (VOC). The mixtures were representative of organic species typically found indoors, but the concentrations tended to be higher than normal indoor levels. Each 4-h experiment was conducted in a controlled environmental facility (CEF, 25 m³) ventilated at ~1.8 h⁻¹. The mixture investigated included 23 VOC (no O₃), O₃/23 VOC, O₃/21 VOC (no *d*-limonene or α -pinene), and O₃/terpene only (*d*-limonene and α -pinene). The net O₃ concentration was ~40 ppb in each experiment, and the total organic concentration was 26 mg/m³ for the 23 VOC mixture, 25 mg/m³ for the 21 VOC mixture, and 1.7 mg/m³ for the *d*-limonene and α -pinene mixture. When the 23 VOC were added to the CEF containing no O₃, no compounds other than those deliberately introduced were observed. When O₃ was added to the CEF containing the 23 VOC mixture, both gas and condensed phase products were found, including aldehydes, organic acids, and submicron particles (140 μ g/m³). When O₃ was added to the CEF containing the 21 VOC without the two terpenes (O₃/21 VOC condition), most of the products that were observed in the O₃/23 VOC experiments were no longer present or present at much lower concentrations. Furthermore, the particle mass concentration was 2–7 μ g/m³, indistinguishable from the background particle concentration level. When O₃ was added to the CEF containing only two terpenes, the results were similar to those in the O₃/23 VOC experiments, but the particle mass concentration (190 μ g/m³) was higher. The results indicate that (i) O₃ reacts with unsaturated alkenes under indoor conditions to generate submicron particles and other potentially irritating species, such as aldehydes and organic acids; (ii) the major chemical transformations that occurred

under our experimental conditions were driven by O₃/*d*-limonene and O₃/ α -pinene reactions; and (iii) the hydroxyl radicals (OH) that were generated from the O₃/terpene reactions played an important role in the chemical transformations and were responsible for approximately 56–70% of the formaldehyde, almost all of the *p*-tolualdehyde, and 19–29% of the particle mass generated in these experiments.

Introduction

Although a variety of volatile organic compounds (VOC) have been found in indoor environments (1–4), their presence is insufficient to explain the prevalence of eye and airway irritation as well as other commonly reported symptoms such as headaches (5, 6). There are other pollutants in indoor environments that have not been adequately characterized (5, 7) and may adversely affect occupant health and comfort.

It has been proposed that reactions in indoor environments between unsaturated VOC and oxidants may produce chemically reactive products that are more irritating to people than their parent compounds and are therefore more likely to be responsible for the symptoms commonly reported in nonindustrial buildings (5–10). Weschler (10) has reviewed recent studies probing indoor chemistry and outlined possible reactions among indoor pollutants in both gas and particle phases. One of the more important reactions is that of ozone (O₃) with terpenes. It has been demonstrated that indoor O₃/terpene reactions produce aldehydes and carboxylic acids and that some of the less volatile products contribute to the growth of fine and ultrafine particles (11–15). Weschler and Shields (13) found a significant increase in the concentration of indoor fine particles when O₃ and terpenes were simultaneously present in a commercial office. Wainman et al. (15) reported a significant formation of fine particles when 20–60 ppb of O₃ was spiked into a simulated room containing a terpene-based air freshener (often found in offices and homes). Long et al. (14) observed a significant formation of ultrafine particles as a consequence of cleaning events, involving mopping floors and cleaning toilets using a pine oil-based cleaner in residential indoor environments.

Besides stable oxidized products, unstable intermediate species such as hydroxyl radicals (OH), alkylperoxy radicals (RO₂), and Criegee biradicals have been reported from the reactions of O₃ with alkenes and terpenes (16, 17). A meaningful quantity of OH was detected following the reaction of O₃ with *d*-limonene in a manipulated office setting (17). It was suggested that OH could further react with other pollutants present indoors to produce species that can adversely affect human health. To date no experimental evidence has been presented in support of this hypothesis, but the clear message is that O₃, a Criteria Pollutant outdoors, has an effect on indoor air quality.

Our laboratories are investigating the health effects associated with exposure to mixtures of VOC and O₃ in the controlled environmental facility (CEF) located at the Environmental Occupational Health Science Institute (EOHSI; 18). In these studies, the net O₃ level is close to 40 ppb, a concentration that can easily be reached indoors during the summer but a concentration not expected to produce acute health effects in the absence of other pollutants (19, 20). The VOC mixture, which is similar to the “Molhave mixture” (18, 21–23), contains 23 chemicals representative of those commonly found in indoor environments but at higher than average concentrations. Detailed information about the VOC

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TABLE 1. Comparison between Concentrations of Individual VOC^a Calculated from Mass Delivered to CEF and Measured by GC/FID

name	CAS Registry No.	C1 (calcd concn, mg/m ³) ^b	C2 (measured by GC/FID, mg/m ³)	% RSD	C2/C1	ppb (v/v) converted from C2
<i>p</i> -xylene	106-42-3	8.3	9.540	18	1.16	2177
<i>n</i> -butyl acetate	105-46-4	8.3	9.320	16	1.13	1944
1-butanol	71-36-3	0.83	0.989	16	1.20	323
<i>n</i> -hexane	110-54-3	0.83	0.983	13	1.19	276
ethylbenzene	100-41-4	0.83	1.035	17	1.25	236
<i>n</i> -hexanal	66-25-1	0.83	0.953	15	1.16	230
<i>n</i> -nonane	111-84-2	0.83	0.996	19	1.21	188
α -pinene	7785-70-8	0.83	0.900	20	1.09	160
1-decene	872-05-9	0.83	0.852	19	1.03	147
<i>n</i> -decane	124-18-5	0.83	0.850	19	1.03	145
ethoxyethyl acetate	111-15-9	0.83	0.787	16	0.95	144
<i>d</i> -limonene	5989-27-5	0.83	0.704	22	0.85	125
2-butanone	78-93-3	0.083	0.087	12	1.05	29
cyclohexane	110-82-7	0.083	0.092	15	1.12	27
4-methyl-2-pentanone	108-10-1	0.083	0.097	12	1.17	23
<i>n</i> -pentanal	590-86-3	0.083	0.070	23	0.85	20
<i>n</i> -propylbenzene	103-65-1	0.083	0.096	18	1.17	19
1,2,4-trimethylbenzene	95-63-6	0.083	0.093	17	1.13	19
<i>n</i> -undecane	1120-21-4	0.083	0.075	18	0.91	12
1-octene	111-66-0	0.008	0.010	20	1.18	2
1,1-dichloroethane	107-06-2	0.83			coeluted with solvent	
<i>n</i> -hexanal	66-25-1	0.83			measured by HPLC/UV method	
2-propanol	67-63-0	0.083			coeluted with solvent	
3-methyl-2-butanone	563-80-4	0.083			coeluted with solvent impurity	

^a Similar to Molhave mixture (27); *d*-limonene was a new addition. ^b Calculated from the mass delivered to the CEF and the air exchange rate.

mixture is presented in Table 1. The exposure studies have been designed to assess potential health effects (e.g., eye, nose, and throat irritation; 18) resulting from both the compounds initially present in the mixture and products of the O₃ initiated chemistry. The present study examines in greater detail the primary and secondary products resulting from the reactions of O₃ with the 23 VOC mixture. The same concentrations of VOC and O₃ have been used as were used in the exposure studies. It was speculated that, among the 23 VOC, terpenes (*d*-limonene and α -pinene) were the key species that drove the chemical transformations; therefore, we further examined the chemical transformations resulting from O₃ with VOC in the presence and absence of terpenes. The conditions tested included (a) 23 compounds (the two terpenes present), (b) O₃ with 23 compounds, (c) O₃ with 21 compounds (absent the two terpenes), and (d) O₃ with *d*-limonene and α -pinene only.

Experimental Methods

Controlled Environmental Facility (CEF). All of the experiments described in this paper were conducted in the CEF without human subjects present. The CEF is a stainless steel chamber in which the temperature, humidity, and air exchange rate are controlled. It is 2.2 m high by 4.1 m wide by 2.7 m deep with a volume of 25 m³ and a surface/volume ratio of 2.1 m⁻¹. The air supply is treated in a series of conditioning processes, which include air cooling/heating, humidification/dehumidification, and filtration through carbon and HEPA filters. The resultant background O₃ concentration is close to zero, and the concentrations of nitrogen oxides are less than 20 ppb (24). The air supply enters the CEF through two diffusers in the ceiling and exits through the perforated stainless steel floor. Constant concentrations of chemical compounds can be maintained in the CEF by injection of the chemicals continuously into the air supply, which flows through the CEF without recirculation. Eight small brushless fans (to prevent unwanted particle generation from brush degradation) are used in the CEF to ensure that the air is well mixed.

For all of the experiments conducted in this study, the CEF was operated at a negative pressure of -0.01 to -0.05 in. of water to prevent leakage of chemicals into the occupied

area. The air exchange rate was measured by monitoring the decay rate of sulfur hexafluoride (SF₆) in the CEF and averaged 1.8 ± 0.2 h⁻¹. The temperature and humidity was maintained in a range from 73 to 78 °F (23–26 °C) and 24–49%, respectively.

Introduction and Measurement of O₃ in the CEF. O₃ was generated in situ by an O₃ arc generator (Ozone Research & Equipment Corporation, Phoenix, AZ). For each experiment, the VOC were first introduced to the CEF. After the VOC reached the desired concentrations, O₃ was injected into the CEF through six ports; this helped to avoid locally high concentrations within the CEF and also achieved good mixing in a short period of time. When the VOC were absent from the CEF, the average O₃ concentration was between 70 and 80 ppb. When the VOC were present in the CEF, the average steady-state O₃ concentration was ~40 ppb. The arc generator used to produce O₃ also generates small quantities of NO and NO₂ (25). The O₃ rapidly oxidizes any NO to NO₂. Given the size of the CEF and the air exchange rates used in this study, NO₂ from the arc generator is expected to contribute less than 10 ppb to the chamber background levels (25).

Ozone concentration was measured using an API model 450 O₃ analyzer (API, Inc., San Diego, CA), which operates on the basis of the principle of UV adsorption. The sensitivity of the instrument was 1 ppb; response time was less than 20 s; and noise was less than 0.7 ppb. The air was sampled at a rate of approximately 1 L/min. The analyzer was calibrated by a U.S. EPA standard method before use and calibrated weekly by a calibrated portable O₃ generator (Thermo Environmental Inc., Model 165, Franklin, MA). A computer was used for recording and processing of the O₃ concentration data every 30 s. The stability of O₃ was monitored for 4 h without VOC present in the CEF. After reaching the designated concentration (~10 min), the O₃ concentration was stable with a variation <10% during the remainder of the 4-h testing period.

Introduction and Measurement of VOC. A syringe pump was used to deliver the liquid VOC mixture to a three-neck 100-mL heated flask. The chemicals were then flash evaporated in the flask and delivered to the CEF by a clean airstream. The airstream containing chemicals was mixed with the main

TABLE 2. Summary of Experimental Conditions

experimental condition	no. of experiments	total VOC (ppm as toluene) ^a	α -pinene (ppm) ^a	<i>d</i> -limonene (ppm) ^a	O ₃ (ppb) ^a	air exchange rate (h ⁻¹)	T (°C)	% RH
CEF background	3	<0.05	nd ^b	nd ^b	<3	1.4–1.8	23–25	24–38
23 VOC-only (no O ₃)	3	6.7–6.9	0.15–0.18	0.12–0.18	<3	1.5–1.8	23–25	24–38
O ₃ /23 VOC	6	6.4–7.0	0.14–0.16	0.10–0.12	40–49	1.6–2.1	23–26	30–47
O ₃ /21 VOC (no terpenes) ^c	2	6.2	nd ^b	nd ^b	40–47	1.6, 1.9	23, 25	39, 46
O ₃ /terpene	2	0.33	0.14	0.11	40–42	1.6, 1.9	23, 24	40, 49

^a Steady-state concentration. ^b nd, not detected. ^c Terpene: α -pinene and *d*-limonene.

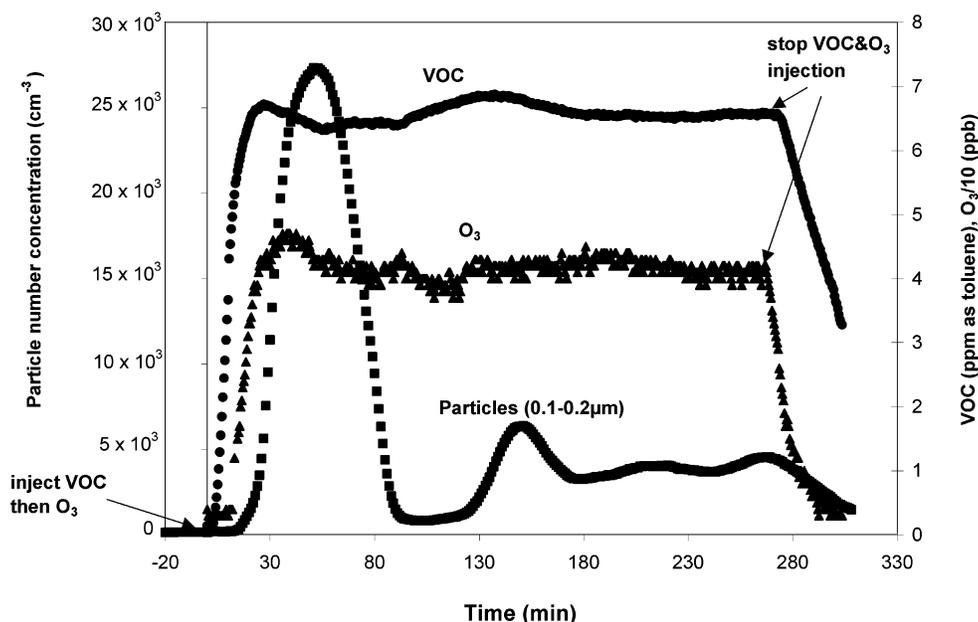


FIGURE 1. Concentrations of O₃, particle number (0.1–0.2 μ m), and total VOC in one of the O₃/23 VOC experiments. VOC injection began first followed by O₃ injection 10 min later. The injections were stopped at 260 min.

clean air supply before entering the CEF through the two air diffusers. The syringe pump was set at a high delivery rate for 7 min in order to reach the designated concentration in a short period of time; a lower delivery rate was then used to maintain constant VOC concentration in the CEF.

To conduct real-time monitoring for VOC concentrations in the CEF, a total hydrocarbon analyzer (THC; Teledyne Analytical Instrument, model 402R, City of Industry, CA) was used, and the total concentration of VOC was reported as a toluene equivalent concentration (23). The THC analyzer was calibrated using methane (CH₄) and toluene gas standards prepared in hydrocarbon-free air (purchased from Scott Specialty Gases, Plumsteadville, PA). The response factor for toluene was 4.2 times of that for CH₄. In addition to measuring the total VOC concentration, the concentrations of individual VOC were determined by a Hewlett-Packard 6890 gas chromatograph equipped with a flame ionization detector (GC-FID, Palo Alto, CA). Air samples from the CEF were collected at ~1 L/min for 2 h on activated charcoal sorbent tubes (20/40, Supelco, Bellefonte, PA). Two VOC samples were collected in the 4-h experimental session. The sample sorbent was placed in a 4-mL glass vial and ultrasonically extracted for 10 min with 2 mL of carbon disulfide; this extraction was repeated a second time. The two extracts were combined and filtered (0.2 μ m PVDF, Whatman). A 2- μ L aliquot was then injected into a GC/FID system for analysis. The GC was equipped with a 30 m \times 0.25 mm i.d. \times 0.25 μ m film DB-5 capillary column (J&W Scientific, Davis, CA). Zero-grade helium (He) was used as the carrier gas at a flow rate of 1 mL/min. The oven temperature program was: 35 °C for 3 min, then ramped to 130 °C at the rate of 10 °C/min, and

held at 130 °C for 1 min. The temperatures for the detector and injection port were 280 and 250 °C, respectively. Calibration standards for all of the compounds were made from authentic samples (>99%, Aldrich, Milwaukee, WI) with chromatography-grade carbon disulfide (CS₂) (Fisher Scientific, Inc., Pittsburgh, PA). For each analysis, a mid-level concentration standard was analyzed to check the precision of the instrument. If the difference between the standard and the calibration curve was larger than 15%, a new calibration curve was established.

The experimental conditions are summarized in Table 2. To be consistent with the controlled exposure study conducted in our laboratories (18), the same VOC concentrations (see Table 1) were used in the present study. For the 23 VOC-only and the O₃/23 VOC experiments, the total VOC concentration was 6.6 ppm as toluene (28 ppm as CH₄); for the O₃/21 VOC experiments, the total 21 VOC concentration was 6.2 ppm as toluene (26 ppm as CH₄); and for the O₃/terpene experiments, the total concentration of *d*-limonene and α -pinene was 0.25 ppm as toluene (1.1 ppm as CH₄). A representative VOC profile from an O₃/23 VOC experiment is presented in Figure 1. A steady-state VOC concentration of 6.6 ppm with a variation less than 10% was maintained throughout the 4-h experiment.

The concentrations of individual VOC measured by GC/FID for the 23 VOC-only experiments are presented in Table 1. 2-Propanol, 1,1-dichloroethane, and 3-methyl-2-butanone were not quantified because they coeluted with either solvent or other contaminants in the sample. The measured VOC concentrations (C₂) were compared with the concentrations (C₁) calculated from the mass delivered to the CEF and the

air exchange rate as shown in Table 1. The ratios for all the compounds ranged from 0.85 to 1.2, and the relative standard deviation among three measurements was <23% for all compounds. The results show that the measured VOC concentrations in the CEF are in good agreement with that predicted from a simple addition process.

Clean air samples (no deliberate addition of either O₃ or VOC) were collected from the CEF. O₃ was close to zero, nitrogen oxides were less than 20 ppb (24), total non-methane hydrocarbons as toluene were less than 0.05 ppm, and only trace amounts of 2-propanol and acetone were found by the GC/FID analysis method.

Measurement of Particles. The number concentrations and size distribution of particles larger than 0.1 μm diameter were measured with an eight-channel LASAIR model 1002 optical particle counter (Particle Measuring Systems, Inc., Boulder, CO) recently calibrated by the manufacturer. The sample flow rate was 0.002 cfm (57 mL/min); this flow rate allowed particle counts to be measured without significantly altering the CEF environment. The eight channels correspond to 0.1–0.2, 0.2–0.3, 0.3–0.4, 0.4–0.5, 0.5–0.7, 0.7–1.0, 1.0–2.0, and >2.0 μm diameter.

The particle mass concentrations were measured using filter-based collection and analysis procedures. Particles were collected on 37-mm Teflon membrane filters using a Harvard sampler (14) with a size cut at 2.5 μm diameter. The sampling head was placed in the center of the CEF. The sampling started after O₃ was introduced to the CEF. The sampling flow rate was ~8 L/min, and the sampling time was 4 h. The sensitivity of the balance used to weigh the filters was 1 μg, and the weighings were performed in a temperature- and humidity-controlled room.

Measurement of Aldehydes and Ketones. Aldehydes and ketones, present in the primary VOC mixture and secondary products, were collected on Sep-Pak C₁₈ cartridges coated with a solution of purified 2,4-dinitrophenylhydrazine (DNPH). The sampling flow rate was ~1 L/min, and the sampling time was 1 h. After being sampled, the cartridge was extracted with 4 mL of acetonitrile (ACN), and a 20-μL aliquot was injected into a Spectra-Physics HPLC/UV system (Reviera Beach, FL) for analysis. The detailed analytical conditions are reported in a previous study (11). The results from the previous study showed that the collection efficiency of the cartridge was greater than 93% and that the limit of detection (LOD) was <0.5 ppb for a sampling volume of 150 L for all identified aldehydes and ketones. The relative standard deviations of the DNPH method was ~15%.

The measured aldehyde concentrations may have been altered by the presence of O₃ in the air drawn through the sampler (ref 26 and references therein). O₃ may react with terpenes on the sorbent to form oxygenated compounds resulting in positive effects. It may also react with carbonyl hydrazones producing negative effects. The data presented in this paper have not been corrected for such potential effects. Additional studies are planned to determine the manner and extent to which O₃ in the sampled air may have influenced the measurements.

Measurement of Carboxylic Acids. Waters Sep-Pak C₁₈ cartridges coated with potassium hydroxide (KOH) were used to collect carboxylic acids. The cartridges were coated in situ with a solution of KOH in methanol according to published procedures (11, 27, 28). The sampling flow rate was set at a constant value between 1.0 and 2.0 L/min throughout an entire experimental run. The sampled cartridges were eluted slowly with 2 mL of HPLC-grade water, and a 100-μL aliquot of the liquid sample was analyzed by the Spectra-Physics HPLC/UV system. The analytical conditions were as follows: 300 mm × 7.8 mm IOA-1000 organic acid analytical column and its guard cartridge (Alltech Associates, Inc., Deerfield, IL); 10 mN aqueous sulfuric acid as the mobile phase eluent

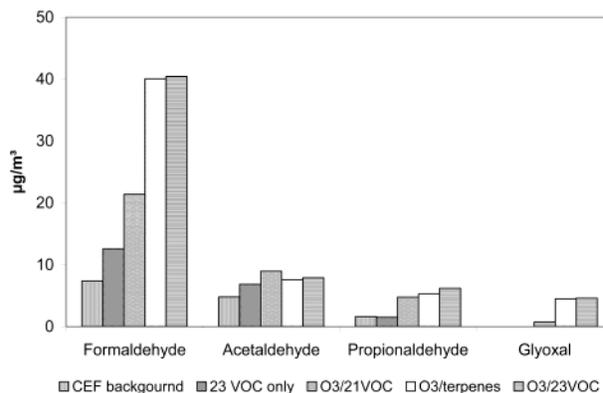


FIGURE 2. Aldehyde concentrations measured under different experimental conditions (no corrections for background).

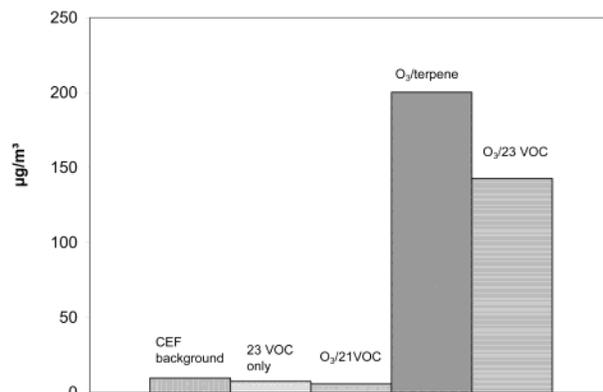


FIGURE 3. Particle mass concentrations measured under different experimental conditions.

solution at a flow rate of 0.55 mL/min; 60 °C column temperature; about 560 psi column pressure; and 210 nm detection wavelength. The standards used were high-purity salts of carboxylic acids (sodium formate and sodium acetate). On the basis of previous studies (11, 28), the KOH-coated cartridge has a collection efficiency for formic acid and acetic acid of >92%. The analytical LOD is 4 ng/100 μL injection, which is equivalent to 0.1 ppb formic acid and 0.4 ppb acetic acid in air for a 360-L sampling volume.

Results

23 VOC-Only Experiments. VOC, aldehydes, organic acids, particle mass, and number concentrations were measured in all of the experiments. For the 23 VOC-only experiments (no O₃), formaldehyde (13 μg/m³) and acetaldehyde (6.9 μg/m³) were slightly higher than the background levels in the CEF (7.4 μg/m³ for formaldehyde and 4.8 μg/m³ for acetaldehyde). This was probably due to oxidation impurities in the liquid VOC mixture (see Figure 2). The concentration of propionaldehyde was 1.5 μg/m³, similar to the background propionaldehyde concentration (1.6 μg/m³). Particle mass concentration was less than 5 μg/m³, which was indistinguishable from the background particle levels in the CEF (see Figure 3).

O₃/23 VOC Experiments. When O₃ was added to the CEF containing 23 VOC at a steady-state concentration of 6.6 ppm as toluene, we observed a number of gas- and condensed-phase compounds that had not been added to the airstream flowing through the CEF. In the humidity range of these experiments (24–49%), there were no differences in the observed products. They included formaldehyde (40 μg/m³), acetaldehyde (7.9 μg/m³), propionaldehyde (6.2 μg/m³), butyraldehyde (6.5 μg/m³), glyoxal (4.6 μg/m³), *p*-tolualdehyde (6.2 μg/m³), and benzaldehyde (3.5 μg/m³). Methyl

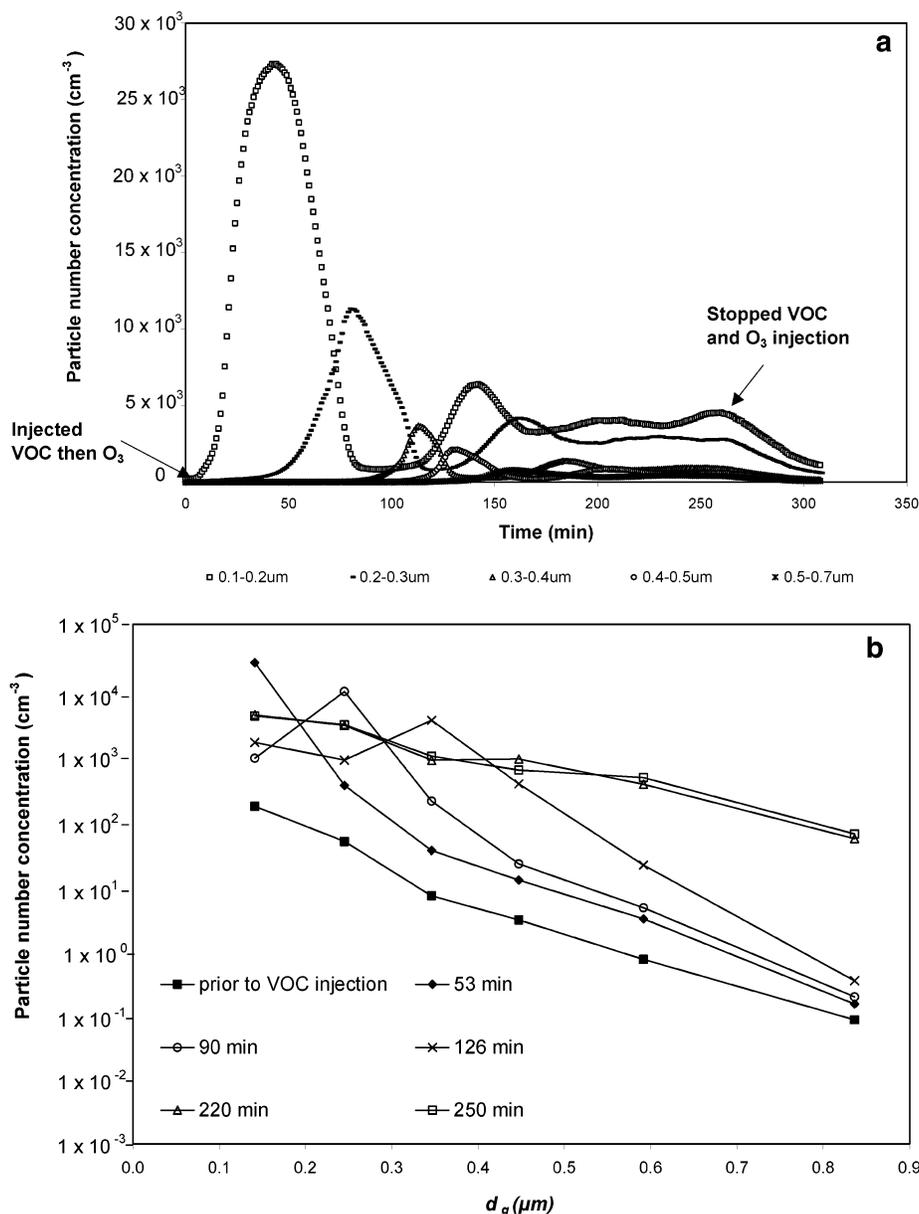


FIGURE 4. (a) Evolution of particle concentrations in different size ranges for one of the $O_3/23$ VOC experiments (42 ppb O_3 ; 6.6 ppm VOC as toluene). (b) Particle number concentrations for different size ranges at selected times in the same (panel a) $O_3/23$ VOC experiment. After 200 min of the ozone injection, the size distribution was relatively stable.

glyoxal was also detected, but it coeluted with a contaminant present in the sample so we were not able to determine its concentration. Organic acids were also measured in the $O_3/23$ VOC experiments; about $13 \mu\text{g}/\text{m}^3$ of formic acid and $6.9 \mu\text{g}/\text{m}^3$ of acetic acid were found.

Besides gaseous species, secondary organic aerosols (SOA) were formed in the $O_3/23$ VOC mixture. As shown in Figure 1, particle concentrations in the size range of $0.1\text{--}0.2 \mu\text{m}$ increased sharply within minutes of adding O_3 to the CEF. The peak concentration (2.5×10^4 particles/ cm^3 for $0.1\text{--}0.2 \mu\text{m}$ sizes) was observed approximately 0.5 h after mixing O_3 with the 23 VOC. Initially, about 80% of the particles $\geq 0.1 \mu\text{m}$ were in the range of $0.1\text{--}0.2 \mu\text{m}$, and almost all the particles were smaller than $1 \mu\text{m}$ (Figure 4a). The size distribution shifted toward larger particle diameters during the course of the experiment. After ~ 3.5 h, the particle size distribution stabilized (Figure 4b). The results are consistent with low vapor pressure reaction products condensing onto or partitioning into existing particles to form larger particles as the experiment progresses. On the basis of gravimetric

analysis of filter samples collected over the 4-h period, the average particle mass concentration was approximately $140 \mu\text{g}/\text{m}^3$. When the injection of VOC and O_3 was stopped, the concentration of particles quickly decreased. The particle decay rate was about the same as air the exchange rate. The decay rate of O_3 (5.2 h^{-1}) was much greater than air exchange rate, reflecting the net effect of air exchange, surface removal, and continued reactions with VOC in the CEF. The VOC decay rate ranged from 1.3 to 1.5 h^{-1} and was slower than air exchange rate, which was probably due to "desorption" of VOC from the walls suppressing the decay of VOC.

$O_3/21$ VOC Experiments. When O_3 was added to the CEF containing 21 VOC (the 23 VOC mixture absent *d*-limonene and α -pinene), most of the products found in the $O_3/23$ VOC experiments were no longer present or present at much lower concentrations in the CEF. The concentration of submicron particles in the $O_3/21$ VOC experiments was at background levels ($2\text{--}7 \mu\text{g}/\text{m}^3$, see Figure 3). Butyraldehyde, *p*-tolualdehyde, benzaldehyde, and methyl glyoxal were not detected. The only products observed were formaldehyde ($21 \mu\text{g}/\text{m}^3$),

TABLE 3. Calculated OH Production Rates and Rate Constants for OH Removal in the CEF

reactant	ppb (v/v)	$O_3 + \text{reactant} \rightarrow \text{OH} + \text{other products}$ $d[\text{OH}]/dt = (\text{yield})k[\text{reactant}][O_3]$			$\text{OH} + \text{reactant} \rightarrow \text{products}$ $-d[\text{OH}]/dt = k[\text{reactant}][\text{OH}]_{\text{indoor}}$	
		rate constant at 23 °C ($O_3 + \text{reactant}$) ($\text{ppb}^{-1} \text{s}^{-1}$)	OH yield	calcd OH production rate (ppb s^{-1})	rate constant at 23 °C (OH + reactant) ($\text{ppb}^{-1} \text{s}^{-1}$)	calcd rate constant for OH removal (s^{-1})
<i>p</i> -xylene	2177				0.35 ^c	766
<i>d</i> -limonene	125	5.1×10^{-6} ^b	0.86 ^b	0.022	4.19 ^c	523
α -pinene	188	2.1×10^{-6} ^b	0.85 ^b	0.013	1.32 ^c	249
<i>n</i> -hexanal	230				0.70 ^g	161
1-decene	147	2.9×10^{-7} ^a	0.18 ^f	3.1×10^{-4}	0.91 ^a	134
1-butanol	323				0.20 ^c	66
<i>n</i> -decane	145				0.29 ^c	41
ethylbenzene	236				0.17 ^c	41
<i>n</i> -nonane	160				0.25 ^c	40
<i>n</i> -hexane	276				0.14 ^c	38
1,2,4-trimethylbenzene	19				0.80 ^c	15
<i>n</i> -pentanal	20				0.70 ^c	14
4-methyl-2-pentanone	23				0.35 ^c	8.0
cyclohexane	27				0.18 ^c	5.0
2-propanol ^h	33				0.13 ^c	4.3
<i>n</i> -undecane	12				0.32 ^c	3.9
<i>n</i> -propylbenzene	19				0.15 ^c	2.8
3-methyl-2-butanone ^h	23				0.12 ^g	2.8
1-octene	2	4.1×10^{-7} ^a	0.18 ^e	5.9×10^{-6}	0.98 ^a	2.0
2-butanone	29				0.03 ^c	0.8
<i>n</i> -butyl acetate	1944				na ^j	na ^j
1,1-dichloroethane ^h	202				na ^j	na ^j
ethoxyethyl acetate	144				na ^j	na ^j
nitrogen dioxide ⁱ	40	7.9×10^{-7}	1	1.3×10^{-3}	0.30 ⁱ	12
formaldehyde	33				0.24 ⁱ	7.9
carbon monoxide ⁱ	1000				5.9×10^{-3}	5.9
methane ⁱ	2000				1.7×10^{-4}	0.3
ozone	40				1.7×10^{-3} ^d	0.1
ethane ⁱ	3				0.01 ⁱ	0.02
surface removal ($k_d(A/V)$) (m s^{-1}) ^k					7×10^{-4}	1.5×10^{-3}
air exchange (E_x) (s^{-1})					5.5×10^{-4}	5.5×10^{-4}

^a Ref 32. ^b Ref 29. ^c Ref 30. ^d Ref 45. ^e Ref 37. ^f OH yield for $O_3/1$ -octene was used for $O_3/1$ -decene. ^g The rate constants for pentanal and 2-pentanone (30) were used for hexanal and 3-methyl-2-butanone, respectively. ^h The concentrations expected in the CEF. ⁱ Refs 24 and 25. ^j Refs 24 and 25. ^k na, not available. ^l Transport-limited deposition velocity (k_d , 0.0007 m s^{-1}) assumed (45). $A/V = 2.1 \text{ m}^{-1}$.

acetaldehyde ($9.0 \mu\text{g}/\text{m}^3$), propionaldehyde ($4.8 \mu\text{g}/\text{m}^3$), and glyoxal ($<1 \mu\text{g}/\text{m}^3$). Except for acetaldehyde, all of the aldehyde concentrations were much lower than those found in the $O_3/23$ VOC experiments (see Figure 2).

O_3 /Terpene Experiments. When O_3 was added to the CEF containing only *d*-limonene and α -pinene, we observed both gas- and condensed-phase products similar to those in the $O_3/23$ VOC experiments. With the exception of *p*-tolualdehyde and benzaldehyde, the aldehyde concentrations were about the same as those in the $O_3/23$ VOC experiments. Particle formation was observed soon after O_3 was introduced to the CEF. Similar particle size distributions were observed, but a higher particle mass concentration ($190 \mu\text{g}/\text{m}^3$) was measured in the O_3 /terpene experiments.

Discussion

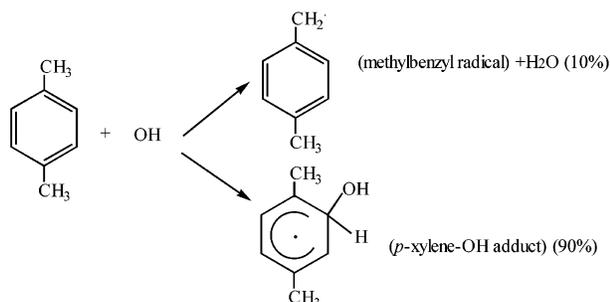
Chemistry in the $O_3/23$ VOC Experiments. The results observed in the 23 VOC-only (no O_3) experiments matched what would be predicted based on a simple one box mass balance model (i.e., the rate of mass delivered to the CEF and the rate of loss by air exchange). No chemical reactions were observed in the CEF. In contrast, the results from the $O_3/23$ VOC experiments indicate that chemical transformations occurred in the mixture at realistic O_3 concentrations and air exchange rates. As reported in the literature (29–32), the second-order rate constant is $5.1 \times 10^{-6} \text{ ppb}^{-1} \text{ s}^{-1}$ for the O_3/d -limonene reaction and $2.5 \times 10^{-6} \text{ ppb}^{-1} \text{ s}^{-1}$ for the O_3/α -pinene reaction (see Table 3). For conditions in which the terpene concentrations (130 ppb for *d*-limonene and 160 ppb for α -pinene) are much greater than that of O_3 (40 ppb), a pseudo-first-order rate constant can be obtained by multiplying the second-order rate constant by the appropriate

terpene concentration. The resulting pseudo-first-order rate constants are $6.4 \times 10^{-4} \text{ s}^{-1}$ for the O_3/d -limonene reaction and $4.0 \times 10^{-4} \text{ s}^{-1}$ for the O_3/α -pinene reaction. These values are comparable to the air exchange rate ($5.0 \times 10^{-4} \text{ s}^{-1}$) in the CEF. The second-order rate constants are $2.9 \times 10^{-7} \text{ ppb}^{-1} \text{ s}^{-1}$ for the $O_3/1$ -decene reaction and $4.1 \times 10^{-7} \text{ ppb}^{-1} \text{ s}^{-1}$ for the $O_3/1$ -octene reaction, both an order of magnitude lower than those for the reactions of O_3/d -limonene and O_3/α -pinene. The CEF concentration of 1-decene (150 ppb) was much higher than that of O_3 while that of 1-octene was much lower (2 ppb). The pseudo first-order rate constants for 1-decene and 1-octene are 4.3×10^{-5} and $1.6 \times 10^{-5} \text{ s}^{-1}$, respectively. Each of these is significantly smaller than the air exchange rate. The reactions of O_3 with the other 19 VOC are so slow (30) that they are of negligible importance given the air exchange rates in the present study. Therefore, in the $O_3/23$ VOC mixture, it is expected that the primary reactions are O_3 with *d*-limonene and α -pinene, followed by O_3 reactions with 1-decene and 1-octene.

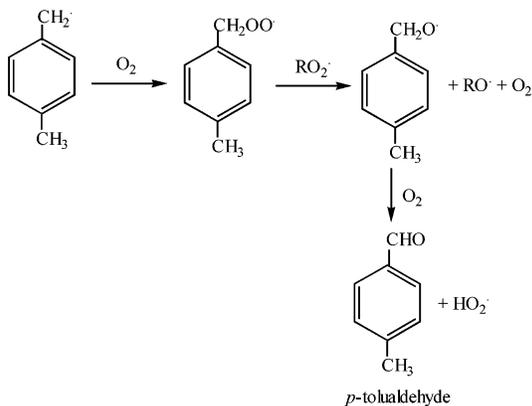
Mechanism of Product Formation. The products observed in the $O_3/23$ VOC experiments are consistent with those reported in the literature for the reactions of O_3 with terpenes and alkenes (29–43). Generally, the mechanisms for reactions of O_3 with *d*-limonene and with α -pinene are similar to those for O_3 with alkenes (i.e., O_3 addition to a $>C=C<$ bond of the terpene to form a primary ozonide). The ozonide will rapidly decompose to carbonyls and Criegee biradicals. Criegee biradicals will react further to form carbonyls, hydroxyl carbonyls, dicarbonyls, carboxylic acids, and oxocarboxylic acids. Formaldehyde is one of the major carbonyl products generated from these reactions, and other

aldehydes, such as acetaldehyde, propionaldehyde, glyoxal, and methyl glyoxal, are minor components generated from the O₃/terpene and O₃/1-decene reactions (35–37, 41, 42). Higher molecular weight compounds with multi-functional groups (e.g., –OH, –COOH, and –C=O groups) have low vapor pressures and are expected to undergo gas-to-particle partitioning resulting in the formation of secondary organic aerosols (34–36, 40–43).

However, some of the products observed in the O₃/23 VOC experiments, such as *p*-tolualdehyde, glyoxal, and methyl glyoxal, cannot be explained via reactions of O₃ with *d*-limonene, α -pinene, or 1-decene. The OH radical, which is among the products of the O₃/terpene and O₃/1-decene reactions, is required to explain the generation of these products in the O₃/23 VOC experiments. For example, the presence of *p*-tolualdehyde indicates that reactions between OH radicals and *p*-xylene occurred in the O₃/23 VOC experiments. As noted above, OH radicals can be generated from O₃/terpene and O₃/1-decene reactions. Although the reaction of O₃ with *p*-xylene is very slow ($<2 \times 10^{-10}$ ppb⁻¹ s⁻¹; 30), the reaction of OH radicals with *p*-xylene is very fast (0.4 ppb⁻¹ s⁻¹; 30). Under the O₃/23 VOC experimental conditions, the overall removal rate for OH via reactions with *p*-xylene was comparable to that with *d*-limonene reflecting the fact that the *p*-xylene concentration was an order of magnitude higher than that of *d*-limonene (see the last column in Table 3). A reaction mechanism for OH/*p*-xylene, producing both gas- and condensed-phase products, has been proposed by Forstner et al. (33) and Tuazon et al. (44). The reaction pathways start with addition to the aromatic ring to form a *p*-xylene–OH adduct and abstraction of a side-chain hydrogen atom to form a methylbenzyl radical:



The methylbenzyl radical reacts rapidly with oxygen to form the methylbenzylperoxy radical. In the absence of nitric oxide, some of the methylbenzylperoxy radicals react with alkyl peroxy radicals (RO₂•) to form *p*-tolualdehyde:



The *p*-xylene–OH adduct undergoes reactions with oxygen to form dimethylphenol, dicarbonyls, and other products. Glyoxal and methylglyoxal were found to be the

major dicarbonyl products of the ring-cleavage process. Glyoxal and methyl glyoxal are also anticipated to be generated from the secondary reactions of OH with high molecular weight carbonyls, such as 4-acetyl-1-methylcyclohexene (limona ketone) and pinaldehyde. The latter two compounds are formed from the reaction of O₃ with *d*-limonene and α -pinene, respectively (35). The mechanisms may involve H-atom abstraction from the tertiary carbons and the carbonyl carbon of the keto-limonoaldehyde (generated from 4-acetyl-1-methylcyclohexene) or pinaldehyde, followed by reaction with oxygen to form alkoxy radicals and acyl radicals. These radicals can further decompose to yield smaller fragments including CH₂CHO, leading to glyoxal and still other compounds. The detailed reaction pathways have been discussed by Grosjean et al. (35).

Organic acids can be formed via the oxidation of aldehydes by OH, HO₂, and RO₂ radicals from the reactions of stabilized Criegee intermediates with water and from the isomerization of Criegee intermediates (ref 11 and references therein). As expected, both formic acid and acetic acid were observed in our experiments.

Estimates of Major Products. On the basis of our current understanding of the relevant mechanisms and kinetics, we attempted to estimate the yield of the major products, including SOA, formaldehyde, and *p*-tolualdehyde, in the O₃/23 VOC experiments.

As discussed above for aldehyde formation, O₃/terpene reactions alone cannot explain the concentration of SOA observed in the O₃/23 VOC experiments. Reactions involving OH radicals must be invoked. The major processes responsible for SOA formation are expected to be reactions of O₃ and OH with terpenes and OH with VOC. Low vapor pressure products from these reactions will subsequently condense/sorb onto existing particles in the CEF forming SOA. We estimate that the rate-limiting steps for SOA formation are the O₃/terpene and OH/VOC reactions themselves. The subsequent condensation/sorption process appears to be much faster. We have reached this conclusion by comparing VOC loss rates at the steady-state O₃ and OH concentrations presented in Tables 3 and 4 with the rate of sorption (0.5 s⁻¹) for the products of the O₃/ α -pinene reaction reported by Kamens et al. (41). Balancing the SOA formation processes are the SOA loss processes—air exchange and wall loss in the CEF. Using a simple one-compartment mass balance model and the sources and sinks presented in Table 4, the SOA concentration in the CEF [SOA] can be estimated using the following equation:

$$d[\text{SOA}]/dt = \sum a_i k_{O_3,i} [\text{O}_3] [\text{VOC}_i] + \sum b_i k_{\text{OH},i} [\text{OH}] [\text{VOC}_i] - E_x [\text{SOA}] - k_{\text{wall}} [\text{SOA}] \quad (1)$$

where a_i is the SOA yield for the reaction of [VOC]_{*i*} with O₃; $k_{O_3,i}$ is the second-order rate constant for the reaction of [VOC]_{*i*} with O₃ (ppb⁻¹ s⁻¹); [O₃] is the O₃ concentration in the CEF (ppb); [VOC]_{*i*} is the concentration of the *i*th VOC (ppb); b_i is the SOA yield for the reaction of [VOC]_{*i*} with OH; [OH] is the OH concentration in the CEF (ppb); $k_{\text{OH},i}$ is the second-order rate constant for the reaction of [VOC]_{*i*} with OH (ppb⁻¹ s⁻¹); E_x is the air exchange rate (s⁻¹), and k_{wall} is the SOA wall loss rate in the CEF. The wall loss rate, 0.2 h⁻¹, was obtained by subtracting the air exchange rate from the observed loss rate for the particle mass as calculated from the particle count concentrations in the size range from 0.1 to 2 μm diameter.

Under steady-state conditions, the SOA concentration is given by

$$[\text{SOA}] = \left(\sum a_i k_{O_3,i} [\text{O}_3] [\text{VOC}_i] + \sum b_i k_{\text{OH},i} [\text{OH}] [\text{VOC}_i] \right) / (E_x + k_{\text{wall}}) \quad (2)$$

TABLE 4. Estimates of Aerosol Concentrations Resulting from the Reactions of O₃ and OH with VOC in the CEF

		Reaction with O ₃ (40 ppb) O ₃ + reactant → SOA + other products				
reactant ^a	ppb (v/v)	rate constant at 23 °C (O ₃ + reactant) (ppb ⁻¹ s ⁻¹) ^b	estd aerosol yield	aerosol concn in O ₃ /23 VOC expts (μg/m ³) ^c	aerosol concn in O ₃ /terpene expts (μg/m ³) ^c	aerosol concn in O ₃ /21 VOC expts (μg/m ³) ^c
<i>d</i> -limonene	125	5.1 × 10 ⁻⁶	0.22 ^d	70	70	
α-pinene	160	2.1 × 10 ⁻⁶	0.19 ^e	32	32	
1-decene	147	2.9 × 10 ⁻⁷	0.01 ^f	0.2		0.2
total aerosol concn from reactions with O₃ (μg/m³)				102	102	0.2
		Reaction with OH OH + reactant → SOA + other products				
reactant ^a	ppb (v/v)	rate constant at 23 °C (OH + reactant) (ppb ⁻¹ s ⁻¹) ^b	estd aerosol yield	aerosol concn in OH/23 VOC expts (μg/m ³) ^c	aerosol concn in OH/terpene expts (μg/m ³) ^c	aerosol concn in OH/21 VOC expts (μg/m ³) ^c
estd OH (ppb)				1.7 × 10⁻⁵	4.5 × 10⁻⁵	2.5 × 10⁻⁷
<i>d</i> -limonene	125	4.2	0.11 ^g	11	30	
α-pinene	160	1.3	0.10 ^g	4.5	12	
<i>p</i> -xylene	2177	0.4	0.03 ^h	4.9		0.1
1-decene	147	0.9	0.09 ^h	2.6		0.0
1,2,4-trimethylbenzene	19	0.8	0.07 ^h	0.2		0.0
<i>n</i> -decane	140	0.3	0.02 ^h	0.2		0.0
<i>n</i> -nonane	156	0.3	0.02 ^h	0.2		0.0
ethylbenzene	236	0.2	0.01 ^h	0.1		0.0
total aerosol concn from reactions with OH (μg/m³)				24	42	0.1
total aerosol concn from reactions with O₃ and OH (μg/m³)				126	144	0.3
measd aerosol concn (μg/m³)				140	190	5.6
% from OH/VOC reaction				19	29	36

^a Contributions to the aerosol yield from the reactions of O₃/VOC or OH/VOC close to or equal zero are not listed in the table. ^b See Table 3 for the references. ^c The air exchange rate was 1.8/h. An average molecular weight of 170 for the condensed phase products was used in the estimation. ^d Ref 36. ^e Ref 42. ^f Ref 37. ^g Calculated from the yield of photooxidation reported by Hoffmann et al. (40) and the percent contribution of OH reaction reported by Griffin et al. (43). ^h Ref 52.

The OH concentration in the CEF can be estimated using the same approach. The major sources of OH are reactions of O₃ with *d*-limonene and α-pinene, and the sinks include reactions with all species present in the CEF. Under steady-state conditions, the OH concentration can be estimated from

$$[\text{OH}] = \frac{(\sum y_i k_{O_3,i} [\text{O}_3] [\text{VOC}_i])}{(E_x + \sum b_r k_{OH,i} [\text{OH}] [\text{VOC}_i] + k_d [A/V])} \quad (3)$$

where *y_i* is the yield of the *i*th O₃/alkene reaction (see Table 3); *k_d* is the OH deposition velocity in the CEF; and *A/V* is the surface to volume ratio within the CEF (2.1 m⁻¹). Even if we assume a transport-limited value for the OH deposition velocity (0.0007 m s⁻¹ (45)), compared with the rate of loss resulting from reactions with VOC in the CEF, the loss of OH radicals by surface removal is of negligible importance (see the final column of Table 3).

Species such as methane (CH₄), carbon monoxide (CO), and nitrogen dioxide (NO₂), which were not measured in the experiments but are generally found indoors and react with OH at a moderately fast rate, are included in Table 3 using typical concentrations reported in the literature (ref 12 and references therein). In the final column of Table 3 we see that the major removal processes for OH radicals are reactions with *p*-xylene and *d*-limonene, followed by reactions with hexanal, α-pinene, and 1-decene. The losses due to reactions with other species, air exchange, and surface removal were minor in comparison. The estimated steady-state OH concentration in the O₃/23 VOC experiments was 1.7 × 10⁻⁵ ppb (4.1 × 10⁵ molecules/cm³).

Substituting this estimated OH concentration and the yields reported in the literature, the SOA concentration in the O₃/23 VOC experiments was estimated using eq 2. The

aerosol mass yields for O₃ and photochemical oxidation reactions have been determined for a large number of terpenes. However, the measured yields for individual organic compound have varied widely (40, 42, 43, 46–48). The yields are influenced by the experimental conditions used in each study (e.g., initial concentrations of the reactants, temperature, and resulting organic aerosol mass concentration (43, 49, 50). For this reason we used yields reported in studies whose experimental conditions were close to our own. The SOA yield from the reaction of only O₃ with α-pinene (no OH radicals or nitrate radicals) has been reported by Yu et al. (42) and Griffin et al. (43) and ranged from 16 to 19% for an initial α-pinene concentration of 31–107 ppb at temperatures between 30 and 36 °C. A yield of 22% was reported by Grosjean et al. (51) for the reaction of O₃ with *d*-limonene. The yields from photochemical oxidations of α-pinene and *d*-limonene have been reported in several studies (39, 40, 43, 47, 48). The values range from ~2% to 40% for the reaction with α-pinene and from 9 to 41% for the reaction with *d*-limonene, generally increasing with initial concentrations of α-pinene and *d*-limonene. In the photooxidation experiments, OH radicals, O₃, and NO₃ radical are all present in the chamber; therefore, the aerosol yields will be the result of products generated via all three oxidation pathways. Recently Griffin et al. (43) has determined the individual contribution of each oxidant (e.g., OH radicals, O₃, and NO₃ radicals) to aerosol formation for the most prevalent biogenic terpenes. The contribution from the reaction of OH with α-pinene was 25% of the total measured photochemical yield. Thus, the estimated maximum yield was 10% for the OH/α-pinene reaction and 11% for the OH/*d*-limonene reaction in these photooxidation experiments. The temperature in our experiments ranged from 23 to 26 °C, which was much lower than those used in the smog chamber experiments, especially the photooxida-

TABLE 5. Estimates of Formaldehyde Concentrations Resulting from the Reactions of O₃ and OH with VOC in the CEF

		Reaction with O ₃ (40 ppb) O ₃ + reactant → HCHO + other products				
reactant ^a	ppb (v/v)	rate constant at 23 °C (O ₃ + reactant) (ppb ⁻¹ s ⁻¹) ^b	estd HCHO yield	HCHO concn in O ₃ /23 VOC expts (μg/m ³) ^c	HCHO concn in O ₃ /terpene expts (μg/m ³) ^c	HCHO concn in O ₃ /21 VOC expts (μg/m ³) ^c
<i>d</i> -limonene	125	5.1 × 10 ⁻⁶	0.10 ^d	5.6	5.6	
α-pinene	160	2.1 × 10 ⁻⁶	0.10 ^e	3.0	3.0	
1-decene	147	2.9 × 10 ⁻⁷	0.53 ^f	2.0		2.0
total formaldehyde concn from reactions with O₃ (μg/m³)				11	9	2.0
		Reaction with OH OH + reactant → HCHO + other products				
reactant ^a	ppb (v/v)	rate constant at 23 °C (OH + reactant) (ppb ⁻¹ s ⁻¹) ^b	estd HCHO yield	HCHO concn in OH/23 VOC expts (μg/m ³) ^c	HCHO concn in OH/terpene expts (μg/m ³) ^c	HCHO concn in OH/21 VOC expts (μg/m ³) ^c
estd OH (ppb)				1.7 × 10⁻⁵	4.5 × 10⁻⁵	2.5 × 10⁻⁷
<i>d</i> -limonene	125	4.19	0.36 ^g	7.1	19	
α-pinene	160	1.32	0.08 ^g	0.6	1.7	
1-decene	147	0.91	0.9 ^h	4.5		0.1
<i>p</i> -xylene	2177	0.35	0.04 ⁱ	1.1		0.0
<i>n</i> -decane	140	0.29	0.05 ^j	0.1		0.0
<i>n</i> -nonane	156	0.25	0.05 ^j	0.1		0.0
ethylbenzene	236	0.17	0.04 ⁱ	0.1		0.0
<i>n</i> -hexane	232	0.14	0.05 ^j	0.1		0.0
total formaldehyde concn from reactions with OH (μg/m³)				14	20	0.1
total formaldehyde concn from reactions with O₃ and OH (μg/m³)				24	29	2.1
measd formaldehyde concn (μg/m³)^k				28	28	8.8
% from OH/VOC reaction for formaldehyde prodn				56	70	4

^a Contributions to the aerosol yield from the reactions of O₃/VOC or OH/VOC close to or equal zero are not listed in the table. ^b See Table 3 for the references. ^c The air exchange rate was 1.8/h. ^d Ref 36. ^e Assumed the same as O₃/*d*-limonene. ^f Ref 37. ^g Ref 48. ^h Ref 54. ⁱ Assumed the same as OH/*m*-xylene (54). ^j Ref 52. ^k The formaldehyde concentration was corrected for that observed in the 23 VOC-only experiment.

tion experiments, most of which were conducted at temperatures ranging from 35 to 49 °C. To estimate the aerosol yield in this study, the maximum yields from the range reported in the literature were used (since lower temperatures result in higher aerosol yields). Yields of 19% and 22% were used for aerosol formation resulting from reactions of O₃ with α-pinene and *d*-limonene, respectively. Yields of 10% and 11% were used for aerosol formation resulting from the reactions of OH with α-pinene and *d*-limonene, respectively (see above). The yields for the reactions of OH with the other compounds and O₃ with 1-decene and 1-octene were taken from Grosjean and Seinfeld (52). An average molecular weight of 170 was assumed for the condensed phase products. The estimated SOA was 102 μg/m³ resulting from the O₃/terpene reactions and 24 μg/m³ resulting from the OH/VOC reactions (see Table 4). The total estimated SOA was 126 μg/m³, which was close to the measured concentration (140 μg/m³). As shown in the fifth column of Table 4, the major reactions contributing to SOA formation were the reactions of O₃/*d*-limonene, O₃/α-pinene, OH/*d*-limonene, OH/α-pinene, OH/*p*-xylene, and OH/1-decene. The contribution from OH reactions accounted for approximately 19% of the aerosol production observed in the O₃/23 VOC experiments.

Using the same approach described for SOA estimation, the concentration of *p*-tolualdehyde was estimated in the O₃/23 VOC experiments. The assumed source of *p*-tolualdehyde was the reaction of OH with *p*-xylene, and the sinks were removal by air exchange, reaction of *p*-tolualdehyde with OH radicals, and wall loss:

$$[p\text{-tolualdehyde}] = \frac{j k_{\text{OH-xyl}} [\text{OH}] [p\text{-xyl}]}{(E_x + k_{\text{OH-tol}} [\text{OH}] + k_{\text{wall}})} \quad (4)$$

where $[p\text{-tolualdehyde}]$ is the concentration of *p*-tolualdehyde in the CEF (ppb); j is the yield of *p*-tolualdehyde from

OH/*p*-xylene reaction; $k_{\text{OH-xyl}}$ is the second-order rate constant for the reaction of OH with *p*-xylene (ppb⁻¹ s⁻¹, see Table 3); $[p\text{-xyl}]_{\text{in}}$ is the concentration of *p*-xylene; $k_{\text{OH-tol}}$ is the second-order rate constant for the reaction of OH with *p*-tolualdehyde (ppb⁻¹ s⁻¹), and k_{wall} is the first-order rate constant for wall loss. Since $k_{\text{OH-tol}}$ is not available, the rate constant for the reaction of OH with benzaldehyde (0.32 ppb⁻¹ s⁻¹) has been used (30). The surface removal rate for *p*-tolualdehyde in the CEF has not been determined. On the basis of the average observed wall loss of polar organic compounds in the CEF, the estimated wall loss of *p*-tolualdehyde was about 10%. Using the yield of 0.08 ± 0.01 reported by Bandow and Washida (53), we estimated the resulting *p*-tolualdehyde concentration in the O₃/23 VOC experiments to be 8.8 ± 2.0 μg/m³. The measured concentration (6.2 μg/m³) is reasonably close to this estimated value.

The concentration of formaldehyde generated by these reactions was also calculated on the basis of the measured O₃ concentration, the estimated steady-state OH concentration, and the appropriate yields reported in the literature (see Table 5). A formaldehyde yield of 10% was reported for the reaction of O₃ with *d*-limonene (36); yields of 36% and 8% were reported for the reactions of OH with *d*-limonene and α-pinene, respectively (48). A similar formaldehyde yield (8%) for the reaction of OH with α-pinene in the absence of NO_x was reported by Noziere et al. (47). Formaldehyde yields resulting from the reactions of O₃ with 1-octene and 1-decene were reported by Grosjean et al. (37) to be about 48% and 53%, respectively. Yields for the reactions of OH with *p*-xylene and other aromatics in this study were assumed to be similar to the value of 4% reported for the reactions of OH with *m*- and *o*-xylene (54). Formaldehyde yields from the reaction of OH with other compounds presented in the CEF were taken from the data reported by Grosjean and Seinfeld (52). Using these yields, the estimated concentration of formaldehyde

in the O₃/23 VOC experiments was 24 μg/m³, which was close to the measured formaldehyde concentration of 28 μg/m³ (the latter value has been corrected for the background concentration found in the 23 VOC-only experiments). As shown in Table 5, the major reactions contributing to formaldehyde formation were O₃/*d*-limonene, O₃/α-pinene, OH/*d*-limonene, OH/α-pinene, OH/*p*-xylene, and OH/1-decene. These calculations indicate that 56% of the formaldehyde production in the O₃/23 VOC experiments was contributed from reactions with OH.

Chemistry in the O₃/21 VOC Experiments. In the O₃/21 VOC experiments, the two terpenes (*d*-limonene and α-pinene) were removed from the 23 VOC mixture. In these experiments, the only initial reactions that were expected to be significant were those between O₃ and 1-decene and between O₃ and 1-octene. Furthermore, given the low concentration of 1-octene (2 ppb), the O₃/1-decene reaction was expected to dominate product generation. The reaction of O₃ with 1-decene occurs at a much slower rate than those of O₃ with *d*-limonene and α-pinene. Hence, the concentrations of products generated from the O₃/1-decene reaction were expected to be much lower than those in the O₃/23 VOC experiments. This expectation was met, and almost no SOA formation was observed in the O₃/21 VOC experiments (see Figures 2 and 3).

The concentration of OH radicals, formaldehyde, *p*-tolualdehyde, and SOA were estimated for the O₃/21 VOC experiments (Tables 4 and 5). The estimated steady-state OH concentration was 2.5 × 10⁻⁷ ppb, which was 2 orders of magnitude lower than that in the O₃/23 VOC and the O₃/terpene experiments. Although the concentration of *p*-xylene was the same as that in the O₃/23 VOC experiments, no *p*-tolualdehyde was observed in the O₃/21 VOC experiments, consistent with the low OH concentration. The production of SOA from the reactions of OH/VOC was negligible, and the total calculated SOA concentration resulting from the reactions of O₃ and OH with the 21 VOC was only 0.3 μg/m³. Only 2.1 μg/m³ of formaldehyde was predicted in the O₃/21 VOC mixture. This estimated value was much lower than that which was observed in the experiments (8.8 μg/m³, background corrected). The reason for this discrepancy is unclear.

Chemistry in the O₃/Terpene Experiments. The O₃/terpene experiments further prove that the O₃/terpene reactions are the dominant chemistry initiators in the O₃/23 VOC experiments. With the exception of *p*-tolualdehyde, similar aldehyde concentrations were observed in both the O₃/23 VOC experiments and the O₃/terpene experiments (see Figure 2). The absence of *p*-tolualdehyde in the O₃/terpene experiments is consistent with the absence of *p*-xylene in the original mixture. The higher SOA concentration observed in the O₃/terpene experiments further demonstrates the important role of OH radicals in these experiments. As presented in Tables 3 and 4, since the O₃/terpene experiments lacked 21 of the VOC present in the O₃/23 VOC experiments, there were many fewer compounds available to react with (or scavenge) OH that was generated from O₃-initiated reactions. As a consequence, the estimated steady-state OH concentration (4.5 × 10⁻⁵ ppb) was higher than that estimated for the O₃/23 VOC experiments. The higher OH concentrations generate more condensable products from the OH/terpene reactions than in the O₃/23 VOC experiments. The estimated SOA concentration in the O₃/terpene experiments was 144 μg/m³, 24% lower than the measured concentration value (190 μg/m³). OH reactions contribute approximately 29% of the aerosol production in the O₃/terpene experiments.

The estimated concentration of formaldehyde was 29 μg/m³ (Table 5) in the O₃/terpene mixture, which was in good agreement with the measured value (28 μg/m³). As presented in the sixth column in Table 5, due to the high concentration

of OH in the O₃/terpene system, almost 70% of the formaldehyde observed in these experiments was derived from the reactions of OH with α-pinene and *d*-limonene.

Implications. This study demonstrates that O₃, at concentrations observed in indoor settings, can initiate reactions in a complex mixture representative of compounds found in indoor air; these reactions generate short-lived highly reactive species (such as hydroxyl radicals) and more stable species (such as aldehydes, carboxylic acids, and submicron particles). Although the compounds present in the mixture are among some of the more commonly observed compounds in indoor air, the concentrations employed in this study tend to be much higher than those observed in nonindustrial indoor environments (1). This is especially true for *p*-xylene and *n*-butyl acetate. These elevated concentrations were used to match those employed in the exposure studies discussed in the Introduction. The air exchange rate used in this study (1.8 h⁻¹) is also somewhat higher than average indoor air exchange rates [approximately 0.65 h⁻¹ (55)]. To some extent the higher air exchange rate compensates for the higher VOC concentrations, but the compensation is only partial. Certain products, such as *p*-tolualdehyde derived from *p*-xylene, are not expected to reach concentrations in most residential homes as high as those observed in this study.

The estimated concentrations for the major products, given the uncertainties in their yield, were in good agreement with those measured in the experiments. This indicates that we do not have large gaps in our understanding of the mechanisms and kinetics involving the reactions of O₃ and OH with the VOC mixtures examined in this study. Furthermore, the results provide striking evidence for the potential importance of the OH radical, which is generated from the reactions of O₃ with unsaturated organics. In contrast to the reactions of saturated organics with O₃, which are too slow to be significant indoors, the reactions between OH and these same compounds are comparable to or faster than typical air exchange rates in commercial and residential buildings. Consequently, by producing OH, the O₃/alkene reactions transform a system where oxidation is thermodynamically favorable but kinetically limited to a system where the kinetic limitation is removed.

Alkenes that exhibit high ozone reactivities (e.g., certain terpenes) are commonly present indoors. Outdoor O₃ can enter these indoor settings, initiating the production of potentially irritating oxidized compounds that are not only present in the gas phase but also contribute to the growth of fine particles. To reduce the production of such undesirable products, it is prudent to limit the use of products that emit high-reactivity alkenes during episodes when outdoor O₃ levels are elevated. However, given the practical difficulties associated with such changes in established use patterns, it is even more crucial to reduce outdoor O₃ levels or to minimize the unimpeded penetration of O₃ from outdoors.

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