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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 2002

Impact Factor: 5.33 · DOI: 10.1021/es015842s · Source: PubMed

Environ. Sci. Technol. **2002**, *36,* 3295−3302

Indoor Hydrogen Peroxide Derived from Ozone/*d*-Limonene Reactions

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In this pilot study, performed in an office manipulated to resemble an environment with a strong indoor ozone source or a significant influx of outdoor air during a smog event, reactions between ozone and *d*-limonene produced hydroperoxides. Hydrogen peroxide (H_2O_2) presumably constituted the majority of the measured hydroperoxides, although a small amount of organic hydroperoxides (ROOH) may have contributed to the signal. Total hydroperoxides were 1.0−1.5 ppb at low air exchange rates (0.5−4 h^{-1}) and 0.6−0.8 ppb at high air exchange rates (12−18 h^{-1}). The net estimated yield ranged from 1.5 to 3.2%, consistent with values reported in the literature. Based on these yields and typical indoor scenarios, peak indoor concentrations of H_2O_2 are projected to be comparable with, but not significantly larger than, peak outdoor concentrations. Hygroscopic secondary organic aerosols (SOA; 10−100 $\mu g\ m^{-3}$) were simultaneously generated by the ozone/*d*-limonene reactions; their co-occurrence with H_2O_2 provides a mechanism whereby H_2O_2 can be transported into the lower respiratory tract. The results demonstrate that reduced air exchange rates lead to increased concentrations of H_2O_2 and SOA as well as a shift in the size-distribution toward larger particles (0.3−0.7 μm diameter), potentially increasing the amount of H_2O_2 delivered to the lower respiratory region. This study increases our understanding of H_2O_2 exposures, including exposures to H_2O_2 associated with co-occurring hygroscopic aerosols. It also re-emphasizes the potential of ozone-driven chemistry to alter indoor environments, often producing products more irritating than their precursors.

Introduction

In 1986 Nazaroff and Cass (*1*) predicted that modest amounts of indoor hydrogen peroxide (H_2O_2) are formed as a consequence of chemical reactions among commonly encountered indoor pollutants. What was not fully appreciated at the time was the potential for indoor chemistry to contribute significantly to the growth of hygroscopic secondary organic aerosols (SOA) and the possible health implications of the co-occurrence of these events since water-containing aerosols can carry hydrogen peroxide into the lower respiratory tract (*2*, *3*).

Atmospheric H_2O_2 is formed primarily through photochemical reactions involving O_3, NO_X, CO, HCHO, and VOCs. The self-reaction of hydroperoxy radicals (HO_2) is a major source of H_2O_2 (*4*). Reactions leading to the formation of HO_2 radicals include the photolysis of O_3 followed by reactions with H_2O and CO (*5*) and the photolysis of HCHO (*4*). The direct reaction of water vapor with intermediates generated in reactions of ozone with alkenes is an additional pathway leading to H_2O_2 formation (*6*−*9*). This latter reaction was not included in the Nazaroff and Cass model of indoor chemistry (*1*); at the time of their study it had not been elucidated. In indoor settings, absent direct sunlight, this ozone/alkene initiated pathway may be the dominant source of H_2O_2.

Reactions between ozone and unsaturated hydrocarbons emitted indoors produce a variety of products, ranging from short-lived highly reactive free radicals to stable, highly oxidized species with low vapor pressures (*10*−*28*). Several recent studies have demonstrated that this chemistry can lead to significant increases in the mass concentration of indoor submicron particles (*14*, *24*, *28*). Increases in the range of 10−40 $\mu g/m^3$ have been reported in indoor settings containing terpene sources and ozone that had been transported from outdoors (*14*, *28*). Presumably, low volatility products of the ozone/terpene reactions adsorb on and absorb in existing particles, contributing to the growth of secondary organic aerosols (*4*, *29*).

Ozone and an alkene must be simultaneously present for reactions between them to influence an indoor setting. Unsaturated hydrocarbons are commonly found in indoor air (*30*−*34*). Sources include cleaning products (*35*), "air fresheners" (*36*), and wood containing products such as cabinets, furniture, and paneling (*37*, *38*). Terpenes such as *d*-limonene, α-pinene, 3-carene, and α-terpinene are an important subgroup of alkenes that are found indoors. They are used as odorants in a variety of consumer products and are also among the active ingredients (e.g., pine oil and dipentene) used in a number of cleaning products (*36*, *39*). Under certain circumstances alkene concentrations indoors can greatly exceed concentrations outdoors. Brown et al. (*30*) and Seifert et al. (*40*) have reported indoor limonene concentrations over 80 ppb. Wainman et al. (*24*) measured *d*-limonene concentrations as high as 175 ppb after applying spray wax to a coffee table for 15 s. Indeed, the odor thresholds for *d*-limonene and α-pinene are greater than 400 ppb (*41*, *38*), and common experience tells us that these compounds, in certain indoor settings, are readily detected by their odor.

In contrast to alkenes, ozone concentrations are normally higher outdoors. The principle source of indoor ozone is outdoor-to-indoor transport; indoor sources include photocopiers, electrostatic filters, and ozone generators. Indoor levels are typically 20−70% of those outdoors (*15*), but can be greater than unity when a strong indoor source is present. The use of ozone for the removal of indoor air contaminants, although of doubtful efficacy, has been widely promoted in the United States. One manufacturer claims to have sold over 2 million ozone-generating devices over the past 12 years (*42*). Ozone generators can elevate ozone concentrations in closed rooms to levels exceeding 2500 ppb (*43*).

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The current paper examines the simultaneous formation of hydrogen peroxide and secondary organic aerosols as a consequence of ozone and *d*-limonene reactions, at low and high air exchange rates and low and moderate relative humidities, in a manipulated but realistic indoor environment. This study should improve assessments of total H_2O_2 exposures, including the contribution of H_2O_2 associated with co-occurring hygroscopic aerosols. It is further hoped that this work will increase awareness of the potential of ozone chemistry to impact indoor environments, often producing products more irritating than their precursors.

Experimental Methods

Offices and Pollutant Generation. Two comparable unoccupied offices (3.1 m × 3.1 m × 3.0 m) were used as the experimental (ozone and/or *d*-limonene) and control (room air only) rooms in this study. These rooms are located on the second floor of a three story building in suburban New Jersey. The rooms were carpeted, had standard office furniture, sealed windows, and dropped ceilings constructed with acoustic tiles; the space above the dropped ceilings was not partitioned. In each room, the door was closed during the experiment. The air exchange rate was 12−18 h^{-1} when the air handling system was operating (designated as high air exchange rates) and 0.5−4 h^{-1} when the system was off (designated as low air exchange rates). A Quantum Series 300 O_3 generator was used to emit O_3 at a rate of 330−2000 μg min^{-1}; its output was adjusted to produce a net ozone concentration of 80−175 ppb. *d*-Limonene was introduced using diffusion vessels. The net *d*-limonene concentration varied with the ozone level and air exchange rate, ranging between 100 and 359 ppb. The diffusion vessels were placed in the room about an hour before turning on the ozone generator and initiating sampling. Experiments were conducted with deliberate introduction of ozone alone ($n = 1$) and *d*-limonene alone ($n = 1$) as well as ozone and *d*-limonene together ($n = 7$) at low (<10%) and moderate (25−35%) relative humidities and low and high air exchange rates. For the experiments conducted at moderate relative humidity ($n = 3$) an ultrasonic humidifier was used to achieve the desired conditions. In such experiments the humidifier was only present in the experimental room, and humidifier operation began the day before the experiment. Particle production from the humidifier was minimized by using 5 megohm deionized, distilled water; background particle levels during humidification were not significantly higher than in the absence of humidification.

Measurements. The air exchange rate was measured by monitoring the dose rate required to maintain a constant concentration of SF_6. Coupled instruments and software provided a continuous value for the air exchange rate throughout a given experiment (SF_6 was measured by a Bruel & Kjaer Type 1302 photoacoustic infrared spectrometer; dosing was accomplished with a Bruel & Kjaer Type 1303 calibrated doser).

The ozone concentration was continuously monitored using a Dasibi Model 1003-AH UV photometric analyzer at a wavelength of 254 nm (range of 0−500 ppb with a precision of ±1% or 1 ppb, whichever is greater).

In each experiment an average *d*-limonene concentration was measured with a passive sampler (OVM 3500, 3M) that collects volatile organic compounds by diffusion to a charcoal sorbent (*44*). One passive sampler was placed near the H_2O_2 collection device (~1 m off the floor) and the other near the window (~1.5 m off the floor). An internal standard (*d*-xylene) was added to the sorbent prior to extraction with 1.5 mL of carbon disulfide. The extract was then analyzed using a Varian Saturn II gas chromatograph/mass spectrometer (ion trap) with a 30 m × 0.25 mm DB5 (0.25 μm film thickness) capillary column. The spectrometer was calibrated with four *d*-limonene standards (0.32−4.0 ng μL^{-1}). The accuracy of this method was approximately 25% at a 95% confidence level.

Real-time particle measurements were made in each room using an eight-channel laser particle counter (Particle Measuring Systems, LASAIR Model 1002). The monitored particle size ranges (optical diameter) were 0.1−0.2 μm, 0.2−0.3 μm, 0.3−0.4 μm, 0.4−0.5 μm, 0.5−0.7 μm, 0.7−1.0 μm, 1.0−2.0 μm, and >2.0 μm. The instrument had a nominal sample flow rate of 50 mL/min and was operated in a continuous sampling mode utilizing 60-s sample intervals.

The relative humidity and temperature were measured using a HOBO data logger (Onset, Pocasset, MA). The HOBO measures temperatures with an accuracy of ±0.7 °C at 21 °C and relative humidity with an accuracy of ±5%.

H_2O_2 was sampled by pulling air at 3 L min^{-1} through two 125 mL gas-washing bottles in series; each contained 50 mL of deionized water. Airborne particles as well as gas-phase species passed through the bubblers; hence the method sampled both gaseous and particle associated H_2O_2. The second gas-washing bottle was used to check for "breakthrough". A dynamic blank (water) and a positive control (standard 2.0 μM solution of H_2O_2) were transported, stored, and analyzed together with the samples. Following collection H_2O_2 samples were stored on ice; triplicate aliquots were analyzed by an automated procedure within 2 h of collection using the method of Lazrus et al. (*45*). Briefly, 30 mg L^{-1} of peroxidase enzyme (horseradish peroxidase Type II) in a fluorescence reagent (0.005 M of *p*-hydroxyphenyl acetic acid (POPHA) and 0.002 M of ethylenediaminetetraacetic acid (EDTA) in 0.01 M of potassium hydrogen phosphate (KH_2PO_4)) was added to the samples. The subsequent reaction products include the dimer 6,6′-dihydroxy-3,3′-biphenyldiacetic acid. This dimer fluoresces at a peak excitation wavelength of 320 nm and a peak emission wavelength of 400 nm. The solution was adjusted to pH 10 by adding 0.05 M of sodium hydroxide to enhance the fluorescence intensity. The hydrogen peroxide concentration is proportional to the fluorescence intensity. A five point calibration was performed with each set of analyses using aqueous H_2O_2 standards (0.25−4.1 μM) prepared from a H_2O_2 stock solution (3%) standardized against a potassium permanganate primary standard. The coefficient of determination (R^2) for the H_2O_2 calibration curve was typically greater than 99%. The detection limit of H_2O_2 was 0.08 μM (0.2 ppb for a sampling time of 180 min) expressed as 3 times the standard deviation of the dynamic blank ($n = 6$). Hydrogen peroxide was below detection limits (0.08 μM) in the dynamic water blank. The measured H_2O_2 concentration in the positive control was 2.07 ± 0.05 μM versus a nominal value of 2.0 μM. There was no hydrogen peroxide loss during transport according to a paired test at the 95% confidence level. The concentration of H_2O_2 in the second bubbler was below detection limits for all experiments. The overall accuracy of the measurements is approximately 5%.

The analytical method just described also measures organic hydroperoxides (ROOH). Hence, the resulting values actually signify total hydroperoxides; in this paper we have adopted the nomenclature H_2O_2* to denote "H_2O_2 + ROOH". Based on mechanistic considerations, the only organic hydroperoxides expected to be produced in measurable amounts in the ozone/limonene system are methyl hydroperoxide and hydroxymethyl hydroperoxide (via ozone's reaction with limonene's double bond external to the ring). Indeed, Hewitt and Kok's laboratory studies of the ozone/limonene reaction, conducted in the presence of a large excess of water vapor, detected only methyl hydroperoxide (*8*). In their studies the gas phase concentration of hydrogen peroxide was roughly three times the gas phase concentration of methyl hydroperoxide; only hydrogen peroxide was detected in the aerosol phase and only hydrogen peroxide

TABLE 1. Summary of Experimental Conditions and Results[c]

sampling date	ozone (ppb)	*d*-limonene (ppb)	RH (%)	air exchange rate (h^{-1})	H_2O_2* (ppb)	total particle number[a] (particles cm^{-3})	total particle mass[a] ($\mu g\ m^{-3}$)
12/16/1999	125	160	<10	high	0.71	10600	17
12/29/1999	100	<1	9	high	0.20	120	0.2
1/13/2000	100	240	28	high	0.80	22000	45
1/19/2000	100	210	5	high	0.58	8200	12
1/27/2000	80	205	6	low	1.2	>25000[b]	>350[b]
2/4/2000	80	360	35	low	1.5	>25000[b]	>350[b]
2/11/2000	<2	270	20	low	<LOD	1500	4
2/15/2000	175	125	11	low	1.0	>25000[b]	> 350[b]
2/16/2000	125	175	30	low	1.3	>25000[b]	>350[b]

[a] Value attained during the final sampling interval of the experiment. [b] Total concentration exceeded measurement limit of the instrument. [c] Total number and mass concentrations are reported for particles in the range of 0.1−1.0 μm diameter. Average sampling time 183 min.

was detected on the walls of the reaction vessel. Based on their laboratory investigations, they concluded that cyclic alkenes produce only hydrogen peroxide. Measurements in outdoor air further support these observations. The gas-phase concentrations of organic hydroperoxides are reported to vary in a diurnal fashion (*8*), with the lowest concentrations observed at night, suggesting that most of the organic hydroperoxides observed outdoors are derived from photochemistry rather than ozone/alkene reactions. In precipitation samples collected at Niwot Ridge the organic hydroperoxides represented 5−20% of the total hydroperoxides; this included both daytime and nighttime events. Based on the above considerations we estimate that the contribution of ROOH to H_2O_2* in the ozone/limonene experiments is less than 10%.

Results and Discussion

Table 1 summarizes the experimental conditions and results for nine experiments that were conducted during the period from December 16, 1999 to February 16, 2000. Late fall and early winter months were deliberately chosen to minimize the contribution of outdoor ozone to indoor levels. In the absence of deliberate generation, ozone concentrations in the offices were consistently below 10 ppb. These experiments were designed to initiate examination of the indoor coproduction of hydrogen peroxide and secondary organic aerosols at varying air exchange rates and relative humidities. Each experiment lasted approximately 3 h, the time required to achieve the desired sensitivity for hydrogen peroxide given the analytical method employed. During the initial hour ozone increased from negligible levels to levels approaching or exceeding 100 ppb. There was significant variability in the average *d*-limonene concentrations during the course of the experiments (125−360 ppb), reflecting the low and high air exchange rates that influenced both the dilution rate and the time available for reaction with ozone. On the other hand, the ozone generation rate was adjusted to keep the average ozone levels fairly constant (80−125 ppb, with the exception of one experiment).

In all nine experiments, H_2O_2* concentrations in the control room—the room without ozone or *d*-limonene— were below detection limits. The experiment on 12/29/1999 was conducted with an ozone source but no limonene source in the experimental room; the concentration of H_2O_2* averaged 0.2 ppb in this room, while it was below detection limits in the control room (see Table 1). Ozone presumably reacted with other species in the room or with species in the bubbler to generate a measurable but small quantity of H_2O_2*. The experiment on 2/11/2000 was conducted with a limonene source, but no ozone source was in the experimental room; the concentration of H_2O_2* was below its detection limit in both the experimental and control rooms. Together, these experiments demonstrate that H_2O_2* levels in the room were negligible if only ozone or only limonene were present. The remaining seven experiments were conducted with simultaneously elevated concentrations of ozone and *d*-limonene. The 3 h-averaged concentrations of H_2O_2* measured in these experiments ranged from 0.6 ppb at a high air exchange rate and low relative humidity to 1.5 ppb at a low air exchange rate and higher, but still low, relative humidity (see Table 1).

TABLE 2. H_2O_2* Concentrations (ppb) Arranged According to the Conditions that Prevailed in the Office during the Period that the Ozone/Limonene Reactions Occurred: Low or High Air Exchange Rates; Low or Medium Relative Humidity[a]

	low RH (<10%)	moderate RH (28−35%)
low air exchange rate (0.5−4 h^{-1})	1.2 (7.3×10^{-5}) 1.0 (4.6×10^{-5})	1.5 (5.2×10^{-5}) 1.3 (5.9×10^{-5})
high air exchange rate (12−18 h^{-1})	0.71 (3.6×10^{-5}) 0.58 (2.8×10^{-5})	0.80 (3.3×10^{-5})

[a] The values within parentheses are the H_2O_2* concentrations "normalized" by the average ozone and limonene concentrations measured during the course of a given experiment (see text for details).

Table 2 is a matrix that places the measured H_2O_2* concentrations into quadrants based on low or high air exchange rates and low or "moderate" relative humidities. Unfortunately, direct comparison of these values is skewed by the fact that the ozone and limonene concentrations in the experiments were not identical. In an attempt to correct for these differences, the average H_2O_2* concentration measured in a given experiment was divided by the average ozone and limonene concentration in that experiment. The resulting "normalized" values are shown in parentheses in Table 2. Regardless of which values are compared, it is apparent that H_2O_2* concentrations are significantly higher at low air exchange rates than at high air exchange rates (according to a paired test at the 95% confidence level). This is anticipated (*46*); at lower air exchange rates there is more time for ozone and limonene molecules to interact before they are swept out of the room. In the case of relative humidity the results are inconclusive. Although the uncorrected H_2O_2* concentrations are slightly smaller at low relative humidity compared with moderate relative humidity, the "normalized" H_2O_2* concentrations display no statistically significant difference with humidity level. Such comparisons are limited by the small number of experiments being compared (three versus four); additional experiments are needed to better define the influence of relative humidity on H_2O_2* production.

Hydrogen Peroxide Yields. The experiments performed in the absence of ozone or limonene demonstrate that the only significant source of H_2O_2 in this office setting was the ozone/limonene reaction. Given this fact, the production of H_2O_2 was expected to be first order in both ozone and limonene (*6*, *7*, *9*). The major sinks for H_2O_2 were air exchange (indoor-to-outdoor transport) and surface deposition. Mind-

TABLE 3. Estimated H_2O_2 Yields Calculated as the Ratio of Measured Values to the Concentration Predicted from a Mass Balance Model (Eq 1)

	low RH (<10%)	moderate RH (28−35%)
low air exchange rate (0.5−4 h^{-1})	2.4%	1.7%
	1.5%	1.9%
high air exchange rate (12−18 h^{-1})	3.3%	3.1%
	2.6%	

ful of the source and sinks, the yield of H_2O_2 in a given experiment was estimated as the ratio of the measured H_2O_2* concentration (see Table 1) to the concentration predicted if the yield were 100%. The latter was calculated from a simple mass balance model derived assuming pseudo-steady-state conditions (*47*). The integrated model has the form

$$[H_2O_2] = k_{rxn}[lim][O_3]/(v_d(A/V) + \lambda) \quad (1)$$

where k_{rxn} is the first-order rate constant for the ozone/limonene reaction at 298 K (5.1×10^{-6} ppb^{-1} s^{-1} (*48*)), v_d is the area averaged H_2O_2 deposition velocity over all surfaces (estimated at 2.5 m h^{-1} (*1*)), A/V is the total surface area within the room divided by the room's volume (2 m^{-1}), and λ is the air exchange rate (estimated as 1 h^{-1} at low air exchange rates and 12 h^{-1} at high air exchange rates). In each 3-h experiment it takes between 20 and 45 min, depending on the air exchange rate, to reach a steady-state H_2O_2 concentration. Since eq 1 assumes steady-state conditions, there is an error in the predicted concentration. Based on modeling simulations we estimate that the resultant error is 4% at high air exchange rates and 12% at low air exchange rates. This error is judged to be small relative to the uncertainty in the other parameters.

Table 3 presents the yields, estimated in this manner, for the seven ozone/limonene experiments. (Note that the yields estimated using eq 1 are, in effect, corrected for H_2O_2 loss to surfaces and air exchange.) Analogous to Table 2, the yields have been placed in quadrants corresponding to different air exchange rates and relative humidities. The yields range from 1.7 to 3.2%, display no obvious variation with relative humidity, and are slightly higher at high air exchange rates.

Becker et al. (*6*, *7*) measured H_2O_2 yields for various O_3/alkene reactions in reactors ranging in size from 130 to 1080 L. For the ozone/limonene reaction they report a yield of 1.8% at approximately 50% RH compared to 0.3% without water vapor. Hewitt and Kok (*8*) measured a yield of 2.1% for the O_3/*d*-limonene reaction in the presence of water vapor. Simonaitis et al. (*9*) report a yield that is roughly a factor of 4 larger than those reported by Becker et al. and Hewitt and Kok. However, they state that, in calculating the yield for the O_3/limonene reaction, they did not use the literature value for the rate constant. Instead, they used their own value which "... was found to be about a factor of 4 lower than the recommended value". If the yield in their study is calculated using commonly accepted values for the O_3/limonene reaction (*48*), then the resulting value is 2.3%, much closer to the values reported by Becker et al. and Hewitt and Kok. The average yield of 2.4% estimated in the present study is in reasonable agreement with the yields reported by Becker et al., Hewitt and Kok, and the reinterpreted value from Simonaitis et al.

Based on the studies of Becker et al. (*6*, *7*) and Simonaitis et al. (*9*), the yield of H_2O_2 is expected to be dependent on the water vapor concentration, assuming that H_2O_2 is formed primarily by the direct reaction of an ozone/limonene reaction intermediate with water vapor. In the experiments performed in the current study, the concentration of H_2O_2* is not significantly higher at moderate relative humidity (28%−35%) than that at low relative humidity (<10%) according to a paired test at the 95% confidence level. It may be that the rate at which H_2O_2 is removed by indoor surfaces increases as the relative humidity increases; this type of behavior has been reported for SO_2 (*49*). However, we have assumed that the deposition velocity for H_2O_2 is close to its transport limit, which would mean that there is little room for variation in this parameter. As noted above, additional studies, especially at higher humidities than could be achieved in these experiments, are necessary to more fully examine the dependence of the resulting indoor H_2O_2 concentrations on the water content of the air.

As shown in Table 3 and noted above, the H_2O_2 yield appears to be slightly higher at high air exchange rates (recognizing that variations in air exchange rates have already been factored into these reported yields). This may simply reflect more time at steady-state H_2O_2 levels at high air exchange rates (i.e., an artifact derived from applying eq 1 to conditions that are not always at steady-state). Alternatively, it may be indicative of competition between water vapor and formaldehyde for an intermediate that leads to H_2O_2 only upon reaction with water. Formaldehyde will compete with water vapor more effectively at low air exchange rates since, as a primary product of the ozone/limonene reaction, its concentration will be significantly higher at low than at high air exchange rates. A competition analogous to that proposed has been demonstrated to occur between water vapor and sulfur dioxide (*7*, *9*).

H_2O_2 and Secondary Organic Aerosols. As noted in the Experimental Section, eight-channel optical particle counters were used to monitor particle counts in both the experimental and control room during the course of these experiments. The final two columns in Table 1 summarize results obtained with these instruments. The mass concentrations reported in Table 1 have been calculated from the number concentrations by assuming that all particles detected in a given size-channel have a diameter equal to the geometric mean of the channel's upper and lower limits and a particle density of 1 g/cm^3. The mass calculated for each channel was then summed to give the total mass. Unfortunately, at low air exchange rates the particle number concentrations exceeded the measurement limits of the laser particle counter's first two channels (0.1−0.2 and 0.2−0.3 μm diameter). Hence these concentrations are simply reported as being greater than the limits of the instrument.

When ozone and limonene were simultaneously present, the particle counts in the experimental room were much higher than in the control room and much higher than they had been prior to the initiation of the experiment. Presumably this increase is a consequence of low vapor pressure limonene oxidation products adsorbing and absorbing to existing ultrafine-particles that subsequently grow into the measurement range of the laser particle counter (*4*, *29*). The resulting particle mass is often referred to as secondary organic aerosol (SOA). There was no significant increase in particle counts when only ozone or only *d*-limonene was present in the experimental room. Under comparable conditions the results reported in Table 1 are consistent with other recent studies reporting significant indoor particle growth as a consequence of ozone/limonene reactions (*14*, *24*, *28*). Indeed, the earlier studies by Weschler and Shields (*14*) were conducted in the same offices as the present study.

Figure 1a shows the particle number concentrations in the first four size-ranges measured in the experimental room on January 13, 2000, a period of high air exchange. Shortly after initiating the experiment, by turning on the ozone generator, there was a sharp increase in the particle counts in the smallest monitored size range (0.1−0.2 μm diameter). The particle number concentration reached a maximum of

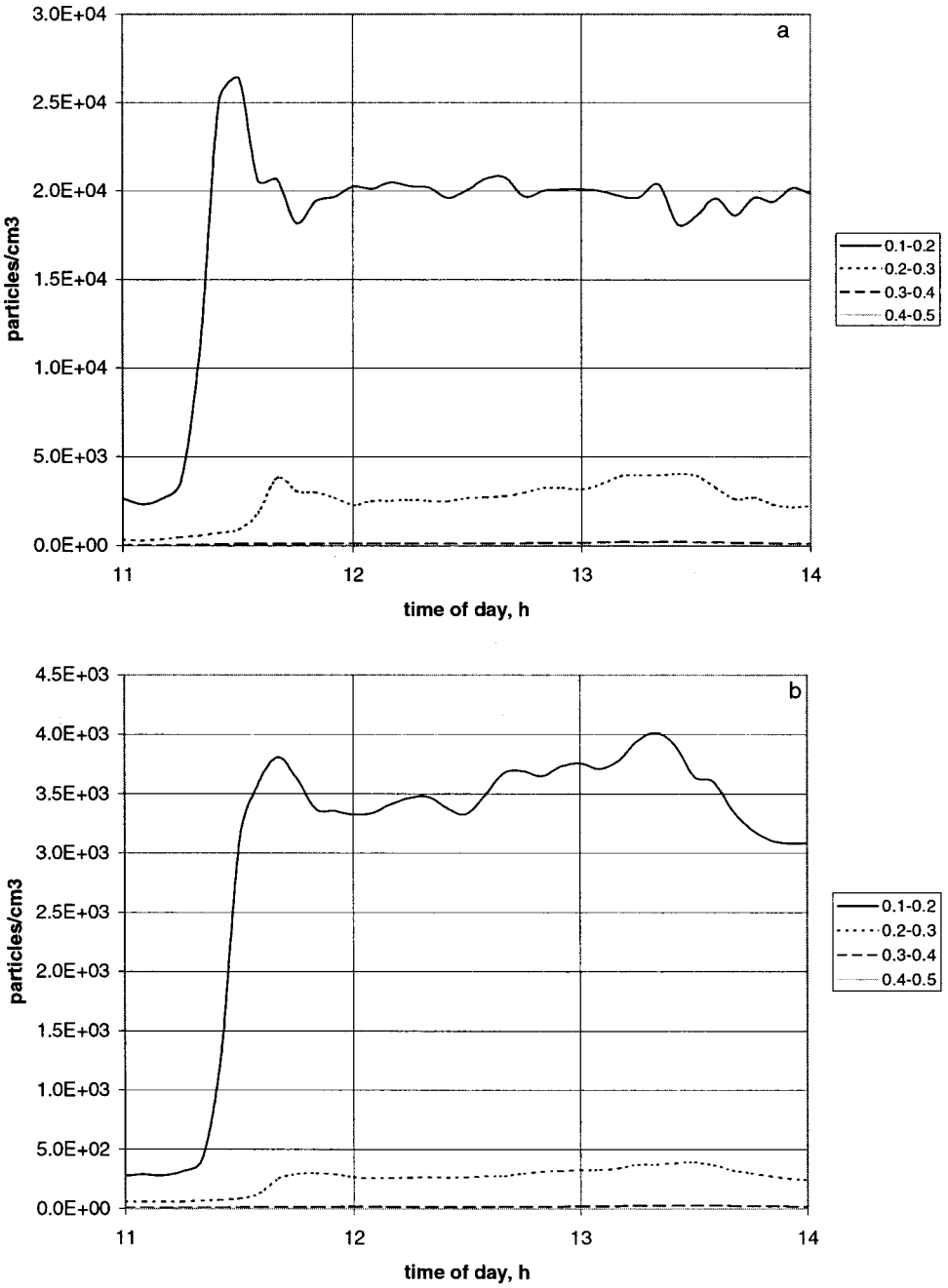

FIGURE 1. Particle number concentrations in the presence of ozone (100 ppb) and *d*-limonene (240 ppb) at moderate relative humidity (RH = 28%) and high air exchange rates on January 13, 2000. Experiment initiated at 11:00 when ozone generator turned on. First four size ranges displayed: 0.1−0.2 μm, 0.2−0.3 μm, 0.3−0.4 μm, and 0.4−0.5 μm diameter. (a) Experimental room and (b) control room.

26 000 particles/cm^3 in the 0.1−0.2 μm size range about 30 min after initiating the experiment; this was followed by a maximum of 3800 particles/cm^3 in the 0.2−0.3 μm size range at about 40 min. There was little growth in the larger size ranges over the course of the experiment.

Figure 1b is analogous to Figure 1a but for the control room. The particle number concentration reached a maximum of 3800 particles/cm^3 in 0.1−0.2 μm size range about 40 min after initiating the experiment, followed by a maximum of 300 particles/cm^3 in the 0.2−0.3 μm size range at about 50 min. There was no detectable growth in the larger size ranges. This increase in particle counts in the control room was presumably due to particle transport from the experimental room to the control room via the nonpartitioned space above the drop ceiling (see below). Under conditions of high air exchange the particle counts in the control room reached values that were about 20% of those in the experimental room.

Figure 2a shows the particle number concentrations in the first five size-ranges measured in the experimental room on January 27, 2000, a period of low air exchange. About 15 min after initiating the experiment the particle counter was "saturated" in its smallest channel (0.1−0.2 μm diameter); after about half an hour the next channel (0.2−0.3 μm diameter) was also saturated. Subsequently the 0.3−0.4 μm diameter channel peaked (without saturating) at 9000 particles/cm^3 at 40 min; the 0.4−0.5 μm diameter channel peaked at 50 min; and the 0.5−0.7 μm diameter channel peaked at about 60 min.

Figure 2b is analogous to Figure 2a but for the control room. In the control room the particle counts remained within the limits of the instrument for all of the monitored

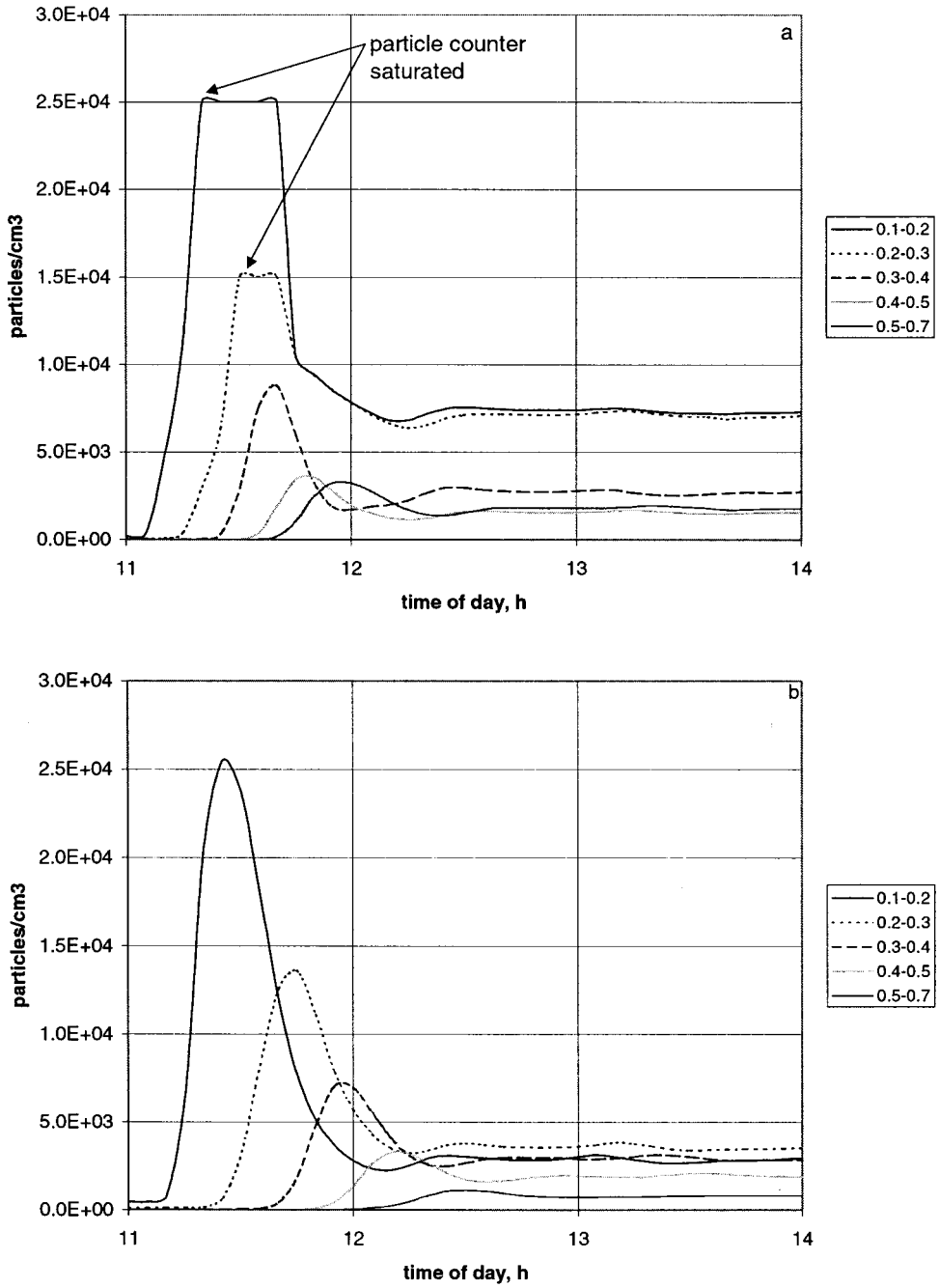

FIGURE 2. Particle number concentrations in the presence of ozone (80 ppb) and *d*-limonene (205 ppb) at low relative humidity (RH = 6%) and low air exchange rates on January 27, 2000. Experiment initiated at 11:00 when ozone generator turned on. First five size ranges displayed: 0.1−0.2 μm, 0.2−0.3 μm, 0.3−0.4 μm, 0.4−0.5 μm, and 0.5−0.7 μm diameter. (a) Experimental room and (b) control room.

size ranges. The particle number concentration reached a maximum of 25 000 particles/cm^3 in the 0.1−0.2 μm size range about 25 min after initiating the experiment, followed by a maximum of 13 600 particles/cm^3 in the 0.2−0.3 μm size range at about 45 min, and a maximum of 7000 particles/cm^3 in the 0.3−0.4 μm diameter at about 60 min; the 0.4−0.5 μm diameter channel peaked at 70 min; and the 0.5−0.7 μm diameter channel peaked at about 90 min. Under conditions of low air exchange the particle counts in the control room reached values that were roughly 80% of those in the experimental room.

Compared with the high air exchange rate experiments, at lower air exchange rates the total particle concentrations were larger, and the size distributions at the end of the 3-h experiments were shifted toward larger particle sizes. Air exchange rates had a much larger effect on particle concentrations than on H_2O_2 concentrations. This contrast is due primarily to differences between these species' deposition velocities, estimated to be ~0.003 cm/s for particles (*50*) and 0.07 cm/s for H_2O_2 (*1*). In the case of submicron particles the rate constant for surface removal is 0.2 h^{-1}, relatively small compared with the air exchange rates in the experiments (0.5−18 h^{-1}). In contrast, for H_2O_2 the rate constant for surface removal is roughly 5 h^{-1}, closer in value to the air exchange rates. Hence, for submicron particles air exchange is the dominant sink and will have a greater influence on concentration than it does for H_2O_2, where surface removal is also an important sink.

The transport of oxidation products between the experimental room and the control room warrants further com-

ment. In designing the experiments we failed to realize that the space above the dropped ceiling was not partitioned. This nonpartitioned space presumably provided a conduit for the transport of both reactants and products from the experimental room to the control room. At high air exchange rates there is a lag of about 10 min between increases in particle counts in different size ranges in the experimental room and the control room. At small air exchange rates the lag is roughly 20−30 min. This difference in lag-time, shorter at higher air exchange rates, argues that the majority of the particles in the control room are present because of transport rather than in situ generation from transported ozone and limonene. Indeed, ozone levels in the control room should have been significantly attenuated by surface removal during transport. Furthermore, in situ production of particles would have been accompanied by in situ production of H_2O_2, yet H_2O_2 concentration were beneath detection limits in the control room under both high and low air exchange conditions. The absence of detectable H_2O_2 in the control room indicates that there was negligible transport of H_2O_2 between the rooms. This is in contrast to what is shown in Figures 1b and 2b for submicron particles and is consistent with a much larger surface removal rate for H_2O_2 than for 0.1−0.7 μm diameter particles (see preceding paragraph).

Implications. Photochemical generation of H_2O_2, a major route to outdoor H_2O_2, is expected to be of little consequence indoors. Outdoor-to-indoor transport is also a negligible source of indoor H_2O_2, due to scavenging by indoor surfaces as evidenced by the negligible transport even between two connected rooms. Apart from certain specialized cleaning products, the major source of indoor H_2O_2 appears to be ozone/alkene reactions. The results presented in this study provide experimental verification that these reactions can lead to ppb-levels of H_2O_2 when alkenes and ozone are simultaneously elevated. Such indoor concentrations are comparable to peak outdoor concentrations, which are in the range of 0.1−5 ppb (*5*). These results can be extrapolated to other commonly occurring indoor conditions using a simple mass-balance model such as eq 1. Significantly, mass balance modeling shows that even when precursor concentrations are high and the air exchange rate is low, indoor H_2O_2 production is somewhat attenuated by its high rate of surface removal, equivalent to an air exchange rate of approximately 5 h^{-1}.

This research was motivated by recent studies suggesting that hydrogen peroxide can contribute to the toxicity associated with atmospheric particulate matter (*2*, *3*). Secondary organic aerosols formed from reactions of ozone with *d*-limonene and other terpenes are comprised of highly polar compounds (*51*, *52*). These aerosols are moderately hygroscopic and have varying amounts of water associated with them, depending on the relative humidity (*53*). H_2O_2 is extremely water soluble; its Henry's law constant is 1×10^5 mol L^{-1} atm^{-1} (*4*). Hence, a fraction of the H_2O_2 produced will partition into aerosol water (*54*). Whereas gaseous H_2O_2 is deposited primarily in the upper respiratory tract due to its high diffusivity (*55*), H_2O_2 absorbed in aerosol water can penetrate deeper into the respiratory tract. This has been confirmed by both modeling studies and experiments with labeled H_2O_2 (*3*).

The partitioning of H_2O_2 between the gas and particle phases depends on the concentration and hygroscopicity of the particles as well as their size. The presence of high concentrations of hygroscopic aerosol is conducive to partitioning of hydrogen peroxide into the particle-phase. During the indoor experiments at high air exchange rates, a large number of particles were produced in primarily the first two monitored size ranges (0.1−0.2 and 0.2−0.3 μm diameter; see Figure 1). During the low air exchange rate experiments, there were a large number of particles produced in the first five size ranges (0.1−0.2 to 0.5−0.7 μm diameter; see Figure 2). Based on the work of Wexler and Sarangapani (*55*), about 90% of the particle-phase H_2O_2 in 0.1−0.2 μm particles evaporates between an airway generation of 15 and 20. The other 10% evaporates and is deposited in an airway generation greater than 20. Slightly larger particles, with smaller evaporation rates, will have greater release of H_2O_2 in the alveolar region (i.e., airway generation > 20). The evaporated H_2O_2 will rapidly diffuse to the surrounding tissue. Even larger particles will retain H_2O_2 longer, and this H_2O_2 will either be deposited or cleared with the same efficiency as the particle. Thus, reduced air exchange produces significantly more particles to serve as H_2O_2 carriers, and the resulting shift in size-distribution toward larger particles favors transport into the alveolar region.

Several biochemical effects have been observed when epithelial cells are bathed in aqueous H_2O_2 solutions (e.g., 20 μM−1 mM solutions, which correspond to 0.2−10 ppb of gas-phase H_2O_2 at equilibrium with an aqueous solution). These include the following: (1) the loss of net active ion transport and integrity of the alveolar cell monolayer (*56*), (2) the loss of intracellular adenosine triphosphate (ATP) and decrease in cellular respiration (*57*), and (3) decreased cell survival after transfer to full growth medium (*58*). The work of Morio et al. (*3*) suggests that exposure to hydrogen peroxide in the presence of atmospheric particles induces tissue injury and that injury is associated with altered production of inflammatory mediators and antioxidants by alveolar macrophages. Experiments were conducted using female Sprague−Dawley rats and ammonium sulfate as a surrogate for atmospheric particles (85% RH; 0, 215, 430 μg/m^3 $(NH_4)_2SO_4$). At 10−20 ppb of H_2O_2 the effects included an increased number of neutrophils in pulmonary capillaries adhered to the vascular endothelium, production of tumor necrosis factor-α by alveolar macrophages, a transient increase in superoxide anion production, a decrease in nitric oxide production accompanied by production of peroxynitrite, and increased expression of the antioxidant enzyme heme oxygenase-1 by stimulated alveolar macrophages. Compared to humans, rats' factor of 10 lower sensitivity to other oxidants (*59*, *60*) suggests that the hydrogen peroxide concentrations in these rat studies are relevant to human H_2O_2 exposures at low ppb levels.

Ozone/alkene reactions produce other reactive species besides the H_2O_2* measured in this study. All ozone/alkene reactions produce free radicals (*4*) including hydroxyl, hydoperoxy, and methylperoxy radicals as well as stabilized Criegee biradicals (*61*). The ozone/1-tetradecene reaction has been shown to produce organic hydroperoxides (*62*, *63*), peroxy-hemiacetals (*63*), and secondary ozonides (*63*). Mechanistic considerations suggest that similar products are formed in various ozone/terpene reactions. The salient fact is that the same chemistry that initiates production of reactive species also initiates growth of submicron airborne particles in the case of higher molecular weight alkenes, especially cyclic alkenes. The co-occurrence of these pollutants provides a potential mechanism— aerosol association— for transport of reactive species into the respiratory tract. Additional studies are necessary to determine the health consequences of exposure to these complex mixtures derived from ozone/alkene chemistry.

Acknowledgments

Research described in this paper was conducted with partial support from the Health Effects Institute (HEI), an organization jointly funded by the United States Environmental Protection Agency (EPA: Assistance Agreement R828112) and automotive manufacturers. The contents of this paper do not necessarily reflect the views of HEI, nor do they necessarily reflect the views and policies of EPA or of motor vehicle and

engine manufacturers. Additional support was provided by Telcordia Technologies, the NIEHS Center of Excellence at EOHSI, and the NJ Agricultural Experiment Station. The use of facilities at Telcordia Technologies and the Environmental and Occupational Health Sciences Institute and the assistance of Drs. Debra Laskin, Lisa Morio, Kimberly Hooper, Paul Lioy, John Reinfelder, Eric Fischer, Brian Buckley, and Mr. Robert Porcja are gratefully acknowledged.

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Received for review December 14, 2001. Revised manuscript received May 13, 2002. Accepted May 23, 2002.

ES015842S