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Measurements of the Hydroxyl Radical in a Manipulated but Realistic Indoor Environment

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Using an indirect technique to obtain a time-integrated signal, we have detected and quantified the hydroxyl radical (OH) in a commercial building. For the purpose of the measurements, the conditions in the office setting were manipulated, but they were representative of conditions that occur naturally. During monitoring periods when the concentrations of both ozone (O_3) and *d*-limonene were elevated and the air exchange rate moderate, we found the average indoor OH concentration to be approximately 7×10^5 molecule/cm^3. This value is lower than typical outdoor midday values ($\sim 5 \times 10^6$ molecule/cm^3) but larger than outdoor nighttime values. The results confirm that reactions among O_3 and olefins can generate meaningful quantities of OH under conditions that commonly occur indoors. In turn, OH initiates a complex series of reactions that generate still other radicals and ultimately produce species that can adversely affect human health and artifacts in indoor environments.

Introduction

Outdoors, oxidation by the hydroxyl radical (OH) determines the lifetimes of many atmospheric constituents. If OH were absent, "the composition of the atmosphere would be totally different and hazardous to many of the present forms of life on Earth" (*1*). Consequently, considerable effort has been expended to measure OH concentrations in outdoor air (*2–7*). Conversely, the concentration of the OH radical indoors has received little attention. Given the absence of direct sunlight indoors, coupled with extremely fast scavenging (by indoor pollutants) of any OH that is transported into a building from outdoors, the *a priori* conclusion is that indoor OH concentrations are negligible. This assumption, however, neglects the possibility that the OH radical can be generated indoors.

We have recently hypothesized (*8*) that indoor OH concentrations can approach those observed outdoors; the primary sources of indoor OH being reactions between ozone (O_3) and unsaturated hydrocarbons. These precursors are common constituents of indoor air; concentrations of both indoor O_3 (refs *9–13* and references therein) and olefinic hydrocarbons (*14, 15*) often exceed 20 ppb. Furthermore, many of the reactions between O_3 and olefinic hydrocarbons occur at rates (*16–21*) fast enough to influence an indoor setting (i.e., the rates are comparable to typical air exchange rates). Our modeling (*8*) indicates that at an air exchange rate of 1 h^{-1}, an indoor O_3 concentration of 20 ppb, and using typically observed concentrations for other key reactants, the steady-state indoor OH concentration is approximately $2 \times$

10^5 molecules/cm^3 ($\sim 10^{-5}$ ppb). The measurements described in the present paper have been designed to test the hypothesis that indoor OH concentrations can approach such levels.

Experimental Section

Indoor Setting. The measurements were designed to monitor OH concentrations in an unoccupied office (3.4 m × 4.0 m × 3.0 m). The room was located on the third floor of a four-story building in suburban New Jersey, approximately 27 air-miles from Manhattan and 6.5 air-miles west of the Atlantic Ocean. The room was carpeted, had acoustic ceiling tiles, and contained standard office furniture. There were no windows in the room, and its door was closed during the monitoring periods.

Air Exchange Rate and Temperature. The air exchange rate (the rate at which the room air was replaced with supply air) was measured by releasing pulses of SF_6 into the room and recording their decay. The decay of SF_6 was monitored using a photoacoustic infrared detection method (Bruel & Kjaer Multi-gas Monitor Type 1302). Temperatures were measured with a Pt 100 air temperature transducer (Bruel & Kjaer Type MM 0034). During the first set of monitoring periods, the air exchange rate varied from 0.64 to 0.81 h^{-1} while the temperature was 28 ± 1 °C; during the second set, the air exchange rate varied from 0.63 to 0.77 h^{-1}, while the temperature was 26 ± 1 °C.

Measurements. The device used in this study for the collection of volatile organic compounds (VOCs), including *d*-limonene, 1,3,5-trimethylbenzene, and perchloroethylene, was a passive sampler, sold by 3M as OVM 3500. The measurement procedure depends on molecular diffusion for eventual contact between vapor phase compounds and the sampler's charcoal sorbent. The sampling rate varies with the diffusion coefficient of the analyte and is typically between 25 and 35 cm^3/min. The reliability of this device has been demonstrated in a number of laboratory and field studies (*22–24*). During each monitoring period, three passive samplers were placed in the room (i.e., the measurements were conducted in triplicate); at the conclusion of a monitoring period, a field blank was also prepared. To reduce measurement errors, an internal standard (1-bromo-4-fluorobenzene) was added to the sorbent prior to extraction with 1.5 mL of carbon disulfide. Organic compounds contained in the extract were separated and identified using a Varian Saturn II gas chromatograph/mass spectrometer (ion trap) containing a 30 m × 0.25 mm DB5 (0.25 μm film thickness) capillary column. The injection port was held at 240 °C while the oven was programmed to rise from 20 to 260 °C. Compound quantitation was achieved using prepared standards of known concentration.

The O_3 concentration within the room was continuously monitored using a Dasibi Model 1003-AH UV photometric analyzer; wavelength, 254 nm; range, 0–500 ppb; precision, ±1% or 1 ppb, whichever is greater. The instrument was interfaced to a personal computer, and data were collected at 1-min intervals.

Dosing. *d*-Limonene, 1,3,5-trimethylbenzene, and perchloroethylene were introduced at a constant rate using either custom or commercial (Dynacal Diffusion Vials from VICI Metronics) diffusion vessels. At 26 °C, the calculated emission rates for *d*-limonene, 1,3,5-trimethylbenzene, and perchloroethylene were 425, 6.3, and 14.9 μg/min, respectively; at 28 °C, the calculated emission rates were 479, 7.1, and 16.7 μg/min. Ozone was introduced using a Quantum Series 300 ozone generator; the emission rates ranged from approximately 330 to 1000 μg/min. For any given monitoring period,

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TABLE 1. Air Exchange Rates, Concentrations (ppbv), and tmb/perc Ratios (ppb/ppb) within the Office during the Five Monitoring Periods[a]

interval	air exchange rate, h^{-1}	[ozone]	[d-limonene]	[1,3,5-trimethylbenzene], [tmb]	[perchloroethylene], [perc]	[tmb]/[perc]
air conditioning season—warmer room (28 °C)						
Aug 30—Sep 6	0.64	62 ± 1	109 ± 3	3.03 ± 0.26	5.51 ± 0.22	0.549 ± 0.036
Sep 6—13	0.81	5.3 ± 0.4	156 ± 7	2.83 ± 0.19	4.31 ± 0.21	0.655 ± 0.015
heating season—cooler room (26 °C)						
Sep 13—20	0.63	106 ± 1	72 ± 8	2.43 ± 0.17	5.11 ± 0.19	0.477 ± 0.029
Sep 20—27	0.77	1.3 ± 0.4	154 ± 5	2.51 ± 0.12	4.19 ± 0.16	0.597 ± 0.011
Sep 30—Oct 7	0.75	192 ± 2	0.10 ± 0.03	2.49 ± 0.08	4.30 ± 0.19	0.580 ± 0.042

[a] During a given monitoring period, the concentrations of d-limonene, 1,3,5-trimethylbenzene, and perchloroethylene as well as the [tmb]/[perc] ratio have been measured with three separate samplers. For each of these values, the tabulated standard deviation is derived from these three independent measurements and is based on an "unbiased" estimate of the variance, obtained by dividing the second moment about the mean by 2 (i.e., $n - 1$) instead of 3 (i.e., n).

the room was given a minimum of 7 h to equilibrate before initiating VOC measurements.

Analytical Procedure

Direct measurements of OH radical concentrations in the range of 10^5-10^6 molecules/cm^3 are extremely difficult (2–7). As an alternative, we devised an indirect method. The approach uses 1,3,5-trimethylbenzene as an indicator—a compound that reacts almost exclusively with OH during the time scale of interest. To determine an average OH concentration in a room, 1,3,5-trimethylbenzene is emitted into the indoor setting at a known rate. (This approach requires that the background level of 1,3,5-trimethybenzene be small enough so as not to interfere with the planned measurements; this was the case for the room in question.) In the absence of OH, the steady-state concentration of 1,3,5-trimethylbenzene can be calculated from its emission rate, the air exchange rate, and the volume of the room; if the measured concentration of 1,3,5-trimethylbenzene is less than this value, the difference is attributed to OH.

1,3,5-Trimethylbenzene reacts with OH much faster than with O$_3$ [5.74×10^{-11} cm^3 molecule^{-1} s^{-1} as compared with 2.20×10^{-21} cm^3 molecule^{-1} s^{-1} (25, 26)]. This preference for OH is crucial to the detection method since O$_3$ is present when we expect OH to be present. At an indoor concentration of 2.5×10^5 molecules/cm^3 (10^{-5} ppb) for OH and 20 ppb for O$_3$, 1,3,5-trimethylbenzene reacts 13 000 times faster with OH than O$_3$.

In the office where we monitored OH, the mechanical ventilation rate ranged from 0.63 to 0.81 h^{-1}, varying with time of day and day of week. These variations complicate attempts to measure OH using changes in the concentration of 1,3,5-trimethylbenzene, since its concentration depends inversely on the air exchange rate. To correct for this perturbation, we released an inert reference compound, perchloroethylene, simultaneously with 1,3,5-trimethylbenzene. Compared to the rate of air exchange, perchloroethylene reacts at a negligible rate with any species that might be present, including OH and O$_3$ (19). Hence, for the conditions in these studies, changes in the concentration of perchloroethylene reflect changes in the air exchange rate as opposed to reaction with OH. If both 1,3,5-trimethylbenzene (tmb) and perchloroethylene (perc) are released at constant rates and the OH concentration is negligible, then the ratio of the concentrations of these compounds (the tmb/perc ratio) remains constant and is independent of variations in the air exchange rate. If the OH concentration is sufficient, on the other hand, the tmb/perc ratio is different from that anticipated in the absence of OH, and the magnitude of the change is a measure of the OH concentration. (Given the second order rate constant for the OH/1,3,5-trimethylbenzene reaction and the air exchange rate, the indoor OH concentration is readily calculated. As an example, at 25 °C and an air exchange rate of 0.75 h^{-1}, a 10% reduction in the tmb/perc ratio, compared with the value when OH is not present, indicates an OH concentration of 4.0×10^5 molecules/cm^3.)

Results

We have used the tmb/perc ratio to measure OH concentrations within a typical office located in a four-story commercial building (see Experimental Section). Conditions within the office were systematically varied from mid-August through mid-October 1996. There were periods when OH levels were expected to be elevated due to the reaction between O$_3$ and d-limonene (an unsaturated hydrocarbon commonly found indoors). There were also periods when OH levels were expected to be much lower since the ozone/limonene reaction was curtailed by reducing the concentration of either ozone or limonene.

Although the concentrations of ozone and d-limonene within the office were manipulated, the conditions were deliberately chosen to mimic conditions that have been reported for actual indoor environments. The ozone emission rates were comparable to those reported for photocopiers (27), and the resulting indoor ozone concentrations were similar to some of the higher values that we have measured indoors in Red Bank, NJ (13), and Burbank, CA (28). The limonene emission rates resulted in limonene concentrations that were higher than average indoor values, but still close to the high-end values that have been measured in various indoor settings (14, 23, 29).

Table 1 summarizes conditions for the monitoring periods, each lasting 6.7 days. These periods are divided into two sets—the first two periods occurred during the air conditioning season, when the room temperature was 28 °C, while the next three periods occurred during the heating season, when the room temperature was 26 °C. (On September 13, 1996, the building's air handling system was switched from air conditioning to heating mode.) An ozone generator was used to add ozone to the office air during three of the five periods (from August 30 to September 6 during the first set; from September 13 to 20 and from September 30 to October 7 during the second set). During the other periods (September 6–13 and September 20–27), the ozone generator was off, and the background concentration of ozone in the office was quite low. This reflects the fact that the majority (>90%) of the supply air was recirculated air, limiting the contribution of outdoor to indoor transport to indoor ozone. Using a diffusion vial, d-limonene was added to the office air during four of the five periods. Diffusion vials were also used to add 1,3,5-trimethylbenzene and perchloroethylene during all five periods (see Experimental Section for the calculated emission rates). The background concentrations of limonene, 1,3,5-trimethylbenzene, and perchloroethylene, measured within the office at the conclusion of the five monitoring periods, were quite low.

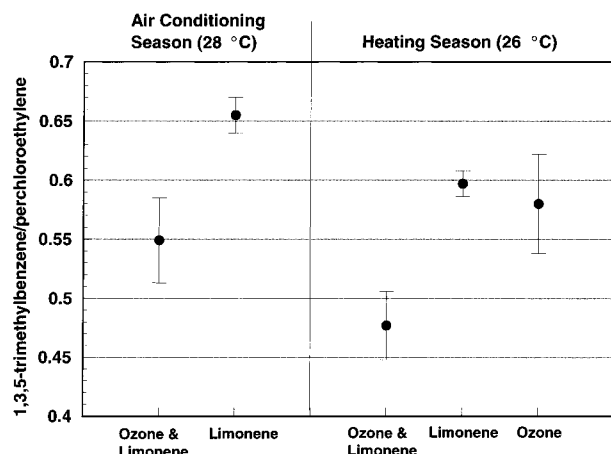The mean concentrations (and standard deviations) of ozone and the relevant hydrocarbons for each monitoring

FIGURE 1. Indoor concentration of 1,3,5-trimethylbenzene divided by that of perchloroethylene (ppb/ppb) for two monitoring periods during the air conditioning season and three monitoring periods during the heating season. Each period lasted 6.7 days. The solid circles and error bars represent means and standard deviations of triplicate measurements, while the labels on the x-axis indicate the compound(s) added to the office air. See Table 1 for air exchange rates and relevant concentrations.

period are listed in Table 1. For ozone, the mean is based on ∼ 640 readings; in the case of the hydrocarbons, the mean is based on triplicate measurements. Note that when the ozone generator was off, the measured VOC concentrations agreed well with steady-state values derived from the calculated emission rates, volume of the room, and average air exchange rate. Also included in Table 1 are the tmb/perc ratios (ppb/ppb) for each of the monitoring periods. This information is displayed graphically in Figure 1. In both sets, that is, during either the air conditioning season or the heating season, the tmb/perc ratio is significantly smaller when ozone and limonene are simultaneously present than when they are not.

During the air conditioning season, the tmb/perc ratio is 0.549 when ozone and limonene are simultaneously present and 0.655 when limonene but negligible ozone is present. This latter tmb/perc ratio is indistinguishable from that expected if OH was not present in the air. Given the average air exchange rate for the period (0.64 h^{-1}), we calculate that the concentration of the OH radical within the office averaged $(6.0 \pm 0.5) \times 10^5$ molecules/cm^3 during the 6.7 days when both ozone and limonene were present.

During the heating season, the tmb/perc ratio is 0.477 when ozone and limonene are simultaneously present, 0.597 when only limonene is added to the air, and 0.580 when only ozone is added to the air. These latter two ratios are indistinguishable from that expected if OH was not present in the air. On the other hand, when both ozone and limonene are present, the tmb/perc ratio is much smaller than when only ozone or only limonene is present. In other words, **both** limonene and ozone must be present to reduce the tmb/perc ratio. (The fact that the tmb/perc ratio was not reduced when O$_3$ by itself was added to the room also demonstrates that the detected OH radicals were not an artifact of O$_3$ generation.) Given the average air exchange rate for the period (0.63 h^{-1}), we calculate that the concentration of the OH radical within the office averaged $(7.1 \pm 0.8) \times 10^5$ molecules/cm^3 during the 6.7 days when both ozone and limonene were present.

Implications

The office experiments outlined in Table 1 differ in several important ways from laboratory experiments that have been conducted to measure OH yields as a consequence of O$_3$/alkene reactions (*30−34*): (i) The office used in the current study is ventilated (∼0.75 h^{-1}), whereas the previously

reported laboratory experiments have been conducted in sealed Teflon chambers. In the office setting, a chemical reaction is of little consequence if it occurs at a rate much slower than the air exchange rate. This constraint does not exist in a sealed chamber. Additionally, ventilation affects the concentration of reactants, intermediates, and products, each of which are continuously purged from a ventilated room. (ii) The steady-state concentrations of limonene and ozone in the office experiments are approximately 10−20 times smaller than the initial concentrations of alkenes and ozone in the chamber experiments; the former are more representative of actual indoor concentrations than the latter. (iii) The office experiments have been conducted using the air common to the building, whereas the chamber experiments used purified air to which the reactants were added. Indeed, the OH radical concentrations measured during the periods when ozone and *d*-limonene were simultaneously added to the office air are approximately one-third the levels predicted if the only chemicals present in the air were those that were added (i.e., ozone, *d*-limonene, 1,3,5-trimethylbenzene, and perchloroethylene). Presumably, other compounds that are naturally present in the office air react with OH at a significant rate, serving as additional sinks. These are likely to include nitrogen dioxide, carbon monoxide, ethanol, formaldehyde, and other VOCs. (iv) The office used in the present study has a much larger volume (41 m^3) than the chambers (6−7 m^3). (v) The office surfaces include carpeting, ceiling tiles, and cloth furnishings, all of which are moderately reactive. Conversely, the chamber surfaces were relatively inert Teflon. For these reasons we feel that one cannot assume that OH radicals will be observed in a room because they have been observed in chamber experiments.

At present, we can only speculate on the importance of the OH radical in indoor environments. Whereas outdoors it has been described as "mother nature's vacuum cleaner" (*35*), indoors its impact is expected to be less benign. In a typical indoor setting, the major reaction partners for OH include *d*-limonene, nitrogen dioxide, ethanol, formaldehyde, carbon monoxide, isoprene, camphene, acetaldehyde, styrene, and the mono-, di-, and trimethyl benzene isomers (*8*). As a consequence of reaction with OH, many of these compounds are transformed into more irritating or corrosive species (e.g., the oxidation of isoprene produces methacrolein and methyl vinyl ketone, while the oxidation of nitrogen dioxide produces nitric acid). Ultimate products of OH-initiated reactions include aldehydes, ketones, alcohols, organic acids, hydroperoxides, organic nitrates, and peroxyacyl nitrates. Arriving at these products is achieved through a complex series of reactions that produce still other radicals (*36*). The overall process has been schematized in Figure 2; the radical intermediates include alkyl radicals (R), alkylperoxy radicals (RO$_2$), alkoxy radicals (RO), and hydroperoxyl radicals (HO$_2$). R and RO radicals react primarily with O$_2$, are short-lived, and do not accumulate to any significant extent; RO$_2$ and HO$_2$ radicals are longer lived (under indoor conditions their lifetimes appear to be on the order of seconds) and are expected to have steady-state indoor concentrations 3−4 orders of magnitude larger than that of OH (*37, 38*). Significantly, when HO$_2$ reacts with NO, O$_3$, or NO$_3$, the OH radical is regenerated; hence, subsets of the reactions shown in Figure 2 constitute chain reactions in which OH radicals are recycled. Through such chains, a single OH radical can oxidize, recycle, and oxidize again, amplifying the impact of indoor OH. (Photolytic reactions have been omitted from Figure 2. Given the absence of direct sunlight, photolysis is expected to have only marginal influence on OH radical chemistry in indoor settings.)

Some of the products of OH-initiated reactions (e.g., methacrolien, nonanoic acid, peroxybenzoyl nitrate) are known to be irritating at very low concentrations (*39*). Some of the products (e.g., hydrogen peroxide, peroxyacetic acid,
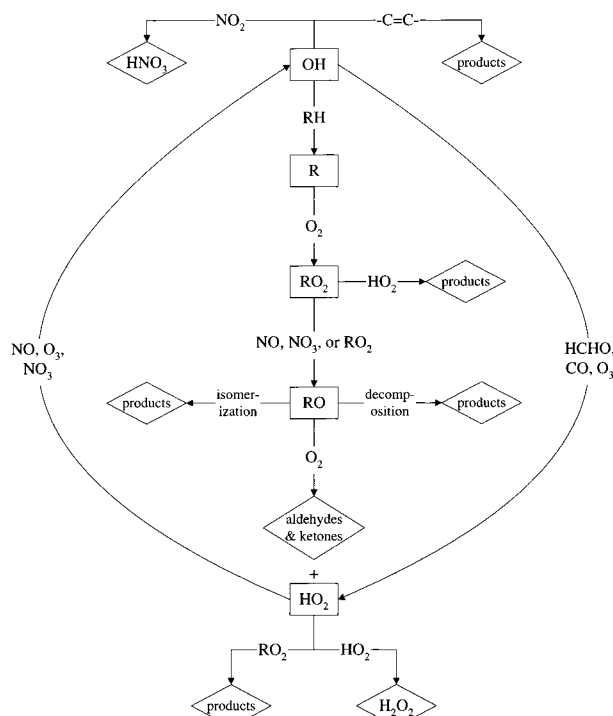
FIGURE 2. Schematic representation of free radicals produced either directly or indirectly as a consequence of reaction between OH and common indoor pollutants. Free radicals are framed with rectangles and stable products are framed with diamonds.

nitric acid) are strong oxidants and/or very acidic compounds that will contribute to oxidative and corrosive processes. In general, indoor OH radicals are expected to adversely affect the comfort and health of human occupants as well as the service life, function, and appearance of their possessions. However, humans have more control over their indoor environments than that outdoors. The concentration of indoor OH can be decreased by limiting the indoor concentrations of its precursors—ozone and unsaturated hydrocarbons. The former is readily removed by charcoal filtration (*40*), while the latter can be reduced through the judicious selection of products that are used indoors.

Acknowledgments

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