Indoor Chemistry: Ozone and Volatile Organic Compounds Found in Tobacco Smoke

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The deliberate generation of ozone in indoor settings has been promoted as a method to reduce the concentration of indoor pollutants. The present study examines the effect of ozone on a subset of volatile organic compounds (VOCs) found in tobacco smoke. The decays of these compounds were measured in a static room-sized chamber: (1) in the absence of ozone, (2) in the presence of moderate ozone concentrations (<0.115 ppm), and (3) in the presence of high ozone concentrations (<1.4 ppm). At moderate ozone concentrations there was little effect on the monitored VOCs. At high ozone concentrations there was a small, unanticipated reduction in the concentration of some of the saturated VOCs, apparently caused by OH radicals produced as a consequence of the ozone/alkene reactions. There was also a much larger reduction in the concentrations of those compounds with unsaturated carbon bonds. However, this reduction was largely matched by an increase in the concentration of a number of aldehydes. Some of these aldehydes are more potent irritants than their precursors. Furthermore, even a relatively small ventilation rate (~0.1 h⁻¹) would produce a greater reduction in the monitored VOCs than that produced by a moderate amount of ozone.

Introduction

In recent years the use of ozone, intentionally produced by an ozone generator, has been promoted as a means to “reduce” the concentration of indoor pollutants. However, reactions between ozone and certain unsaturated organic compounds in indoor environments have been shown to generate products that are more reactive and/or irritating than their precursors. This paper examines the effect of ozone on the concentration of volatile organic contaminants from a specific source—smoking. The experiments have been conducted in a room-sized environmental chamber intended to represent a simple indoor environment.

There are literally hundreds of different volatile organic compounds (VOCs) present in environmental tobacco smoke (ETS). In this study we have chosen to monitor 18 of these compounds. They have been chosen because they are some of the more abundant organic constituents of ETS and because they are representative of the different types of compounds known to be present. Based on their expected behavior in the presence of ozone, we have assigned these VOCs to one of three groups: Group I—compounds that neither react with ozone at a significant rate nor are ozone reaction products; Group II—compounds that react with ozone at a rate comparable to or faster than typical air exchange rates; Group III—compounds that do not react with ozone at a significant rate but are among the products of the reaction of ozone with other compounds found in tobacco smoke. Figure 1 lists these compounds by group and displays their structures. In addition to the separately monitored VOCs, we have also monitored an undifferentiated signal produced by the sum of the VOCs present in the chamber.

Experimental Section

Chamber. Experiments were conducted in a modified Association of Home Appliance Manufacturers (AHAM) AC-1 chamber (11). The chamber dimensions are 3.66 x 2.83 x
2.41 m for a total volume of 25 m³. The interior surfaces consist of wallboard with linoleum flooring per the AHAM specifications. The chamber is flushed using a single pass ventilation system with a 150 m³/min fan drawing air from the room. Inlet air passes through a 60% efficient prefilter, a carbon filtration slide-pak, and finally a HEPA filter. During the experiments the chamber was operated in static mode; that is, there was no forced ventilation. The chamber air exchange rate was measured on three occasions using standard carbon dioxide decay techniques. The results were 0.018, 0.019, and 0.018 air changes/h (h⁻¹). A ceiling fan in the chamber was operated at low speed during testing to prevent stratification. Initial mixing of the smoke was facilitated by the use of an oscillating table fan positioned on the floor.

**Ozone Generator.** A commercially available appliance was used to generate ozone. This device produces a corona discharge on wire mesh screens connected to a high-voltage power supply. It is equipped with a fan that pulls air from the back of the unit, across the wire mesh screens, and out the front of the unit. This fan was operated at a high setting (0.17 m³/s) for all tests. The device has a dial that alters the voltage to the wire mesh screens. The dial is circumscribed by markings indicating recommended settings based on the floor area of the room in which the device operates. For purposes of these tests, the device was operated in two modes: “room setting”, the manufacturer’s recommended setting based on the floor area of the chamber, and “high setting”, the dial at its maximum position. Ozone concentrations increased exponentially over the duration of a 5-h experiment; at the “high setting” ozone levels within the chamber increased exponentially over the duration of a 5-h experiment. Ozone concentrations at high ozone concentrations were not corrected for this positive artifact; the increases reported for ozone concentrations (wavelength, 254 nm; range 0.001–5 ppm; precision ±3% of the reading). Three point calibrations were performed each week of testing.

**Procedure.** For each set of experiments, the test chamber was sealed, and the filtration/air-recirculation loop was turned on for a minimum of 60 min. The filtration/air recirculation system was then shut off, and the smoke of four unfiltered research cigarettes (IR4 from the Tobacco and Health Research Institute, University of Kentucky) was delivered to the chamber. This was accomplished by passing filtered air through the lit cigarette into a glass container and finally into the chamber through stainless steel tubing. After a brief mixing interval, “initial” VOC and aldehyde samples were collected. The ozone-generating device was then turned on (except for “no ozone” experiments); this point was considered time zero. Additional samples were collected at 1 h, 2.5 h, and 5 h after time zero. A total of nine experiments were conducted: three no ozone experiments, three experiments at moderate ozone concentrations, and three experiments at high ozone concentrations. In several experiments background VOC samples were collected prior to smoke injection. For the 18 compounds monitored in this study, background levels were negligible compared with the levels measured following the injection of smoke.

**Results and Discussion**

The initial concentrations of the 18 constituents of ETS monitored in this study vary greatly; the levels range from lows of 2.5 and 3.0 µg/m³ for decanal and nonanal to highs of 360 and 650 µg/m³ for isoprene and acetaldehyde. The average initial concentrations of the monitored VOCs are shown in Table 1. This table also summarizes changes, as percent of initial concentration, of the monitored VOCs in the presence of different ozone concentrations both 2.5 and 5 h after the experiments were initiated.

**No Ozone.** As can be seen in Table 1, even when the ozone generator is not operating, most of the Group I and II compounds display a decrease in concentration over the course of the experiments (isoprene and 2,5-dimethylfuran are the exceptions to this statement). Some of this decrease is due to the chamber’s modest air exchange rate (0.018 air
changes/h). Theoretically, this air exchange rate should produce about a 5% decrease after 2.5 h and a 10% decrease after 5 h. However, some of the Group I and II compounds decrease by percentages greater than these values during the no ozone experiments. The larger decreases are due, in part, to sorption on chamber surfaces. The results in Table 1 suggest that, among the Group I and II compounds, sorption is greatest for pyridine, pyrrole, and 2-furancarboxaldehyde. These are the most polar compounds in Groups I and II, and, hence, these compounds are expected to have the greatest affinity for the chamber’s surfaces.

Figure 2 shows the initial (t = 0) and final (t = 5 h) mass concentrations for the 18 monitored VOCs when there is no ozone in the chamber (i.e., ozone generator not operating). With the exception of isoprene, the small decreases noted above are apparent for the first 12 compounds in Figure 2. In the case of the last six...
compounds, the Group III compounds, there is a decrease in the concentration of acetaldehyde, little change in the concentration of benzaldehyde, and increases in the concentrations of formaldehyde, hexanal, nonanal, and decanal. The most likely cause of these increases is autoxidation \((O_2)\) of unsaturated hydrocarbons, including fatty acids, known to be present in ETS \((20, 21)\). Note that hexanal, nonanal, and decanal had initial concentrations less than 5 \(\mu g/m^3\), so that it does not require much of an absolute increase in concentration to produce a large relative increase. A small amount of acetaldehyde is also likely produced by autoxidation, but the small amount produced is overwhelmed by the amount lost to surface sorption and air exchange. The latter losses are large, in an absolute sense, since acetaldehyde has a large initial concentration.

**Moderate Ozone.** Figure 3 is analogous to Figure 2 but shows composite results when the ozone levels are moderate. When the ozone-generating device is operated at a moderate setting, the reduction in the concentration of Group I compounds is nearly identical to that observed when the ozone generator is not operating (Figures 2 and 3, Table 1). As noted above, the decay is primarily a combination of sorption on the chamber surfaces and air exchange. In the case of the Group II compounds, their decrease is somewhat greater in the “moderate ozone” experiments than in the no ozone experiments; this is true both 2.5 and 5 h into the test. Comparing Figures 2 and 3 \((t = 5\) h), the larger decreases are most apparent for isoprene and d-limonene. The effect of moderate ozone on the concentration of Group III compounds is also small but in the opposite direction from that observed for Group II compounds. Formaldehyde and benzaldehyde show distinct increases in their concentrations compared with the no ozone conditions. The small increases in the concentrations of these compounds are matched by small decreases in the concentrations of isoprene, d-limonene, and styrene at moderate ozone levels. Acetaldehyde's concentration at 5 h has not decreased as much in the presence of moderate ozone as in the no ozone case. Its concentration at 5 h is actually 30 \(\mu g/m^3\) larger with moderate ozone than with no ozone, consistent with increased acetaldehyde production. None of the Group II compounds are expected to produce acetaldehyde upon reaction with ozone; other unsaturated organic constituents of the ETS must serve as precursors for the acetaldehyde.

**High Ozone.** Figure 4 shows composite results for concentrations of the 18 monitored VOCs when the ozone levels are high. Under these conditions, the decreases observed in the concentrations of the Group II compounds and the increases in the concentrations of the Group III compounds are quite large. Even the compounds in Group I display a slightly larger decrease in concentration in the presence of high ozone levels than in the presence of either no ozone or moderate ozone (see Table 1). Based on the very slow rate at which these compounds react with ozone (see Kinetics subsection and Table 2), the decreases observed in the Group I compounds cannot result from the direct reaction with ozone. Instead, we hypothesize that the reductions are due to reactions with hydroxyl radicals produced as a consequence of ozone reacting with Group II compounds and other unsaturated compounds present in ETS.

Based on the measured net reductions (“high ozone” case corrected for the natural decay measured in the no ozone case) in the concentrations of benzene, toluene, m,p-xylene, o-xylene, and ethylbenzene and the reported rate constants for the reactions between these compounds and the hydroxyl radical, we have calculated the necessary hydroxyl radical concentration to effect such a reduction during the high ozone experiments. The result is \((9 \pm 8) \times 10^{-5} \text{ ppb OH}\). The production of the hydroxyl radical in indoor settings as a consequence of ozone/alkene chemistry has been discussed in recent studies \((4, 5)\). The magnitude of this calculated hydroxyl concentration for the high ozone chamber experiments is consistent with that expected based on the estimated sources and sinks of \(\text{OH}\) during the high ozone experiments.

**FIGURE 3.** Initial and final concentrations for the monitored constituents of environmental tobacco smoke. Ozone generator at moderate setting.
on the order of 10^{-4} ppb using an approach similar to that discussed in ref 4).

Note that the pyridine reduction is apparently smaller at the “high setting” than at the “room setting”; at the high setting polar ozone/alkene reaction products (aldehydes, ketones and organic acids) may be displacing pyridine from sorption sites on the chamber surfaces, but additional experiments would be necessary to test this hypothesis.

Turning to the Group II compounds, when the ozone generating device is operated at the high setting, within 2.5 h the initial concentration is reduced by 90% or more for 2,5-dimethylfuran, pyrrole, and d-limonene (see Table 1). By 5 h all of the compounds in Group II, with the exception of 2-furancarboxaldehyde, have been reduced in concentration by more than 95%. The percent changes in the concentrations of Group III compounds are also large but opposite from those observed for the Group II compounds. The formaldehyde concentration has increased by 1400% at 2.5 h and by 2500% at 5 h. Formaldehyde is one of the products directly formed by the reaction of ozone with isoprene, styrene, and d-limonene. At the high setting, the amount of formaldehyde produced (500 µg/m^3 or 405 ppb) is greater than the net reduction in the concentration of isoprene, styrene, and d-limonene (485 µg/m^3 or 152 ppb), suggesting that other ETS constituents with terminal double bonds also react with ozone to produce formaldehyde. Benzaldehyde is a direct product of the ozone/styrene reaction. The increase in the concentration of benzaldehyde at the high setting (23 µg/m^3 or 5.3 ppb) is matched by the decrease in the concentration of styrene (24 µg/m^3 or 5.6 ppb). Acetaldehyde is the only Group III compound that does not display a sharp increase at high ozone. However, acetaldehyde’s concentration is, on average, 100 µg/m^3 greater at t = 5 h in the high ozone experiments than in the no ozone experiments.

**Kinetics.** The results presented in Table 1 and Figures 2–4 are anticipated, based on the rate constants reported in the literature (or estimated) for gas-phase reactions between ozone and the 18 monitored ETS constituents (22–28). Table 2 summarizes such rate constants. Ozone is known to react with the Group I and III compounds very slowly (second-order rate constants smaller than 10^{-20} cm^3 molecule^{-1} s^{-1}). In the presence of 0.050 ppm of ozone, these compounds have half-lives longer than 16 000 h (95 weeks). Hence, reactions between ozone and Group I and III compounds
are too slow to be of any practical consequence in indoor settings. Table 2 also lists the calculated percent changes in the concentrations of the monitored VOCs after 2.5 and 5 h at both moderate and high ozone settings. The calculated reductions compare reasonably well with the measured reductions (correcting the values in Table 1 for the percent change observed in the absence of ozone). Of the Group II compounds, d-limonene reacts with ozone the fastest, and, indeed, it displays the largest reductions when the moderate and high ozone results are compared to the no ozone results (see Table 1 and Figures 2–4). Of the Group II compounds, 2-furancarboxaldehyde reacts with ozone the slowest, and the percent reductions at moderate and high ozone levels reflect this. (Rate constants have not been reported for the reaction of ozone with either 2-furancarboxaldehyde or 2,5-dimethylfuran. However, based on the reported ozone/furan rate constant (25), and the properties of the substituent groups, rate constants have been estimated.) The other Group II compounds react with ozone at rates between that of d-limonene and 2-furancarboxaldehyde, and the measured results reported in Table 1 are consistent with this. Note that a large fraction of the reduction observed for pyrrole in the moderate ozone experiments is due to some process other than homogeneous reaction with ozone; sorption to chamber surfaces may play a role. It should also be noted that heterogeneous oxidation of selected adsorbed compounds may enhance the overall destruction rate over that predicted based solely on homogeneous rate constants. However, the reasonable agreement between the calculated homogeneous changes reported in Table 2 and the measured changes in Table 1 indicates that heterogeneous processes do not contribute order of magnitude increases in the oxidative effects of ozone.

The final column in Table 2 shows the equivalent ventilation rates that would be needed to remove a given compound at the same rate as 0.050 ppm of ozone. The equivalent ventilation rates have been calculated assuming that the ozone concentration is significantly larger than that of the ETS constituent and calculating a pseudo-first-order rate constant (in units of h⁻¹) at a concentration of 0.050 ppm ozone. A ventilation rate as small as 0.1 h⁻¹ removes the monitored VOCs, with the exception of d-limonene and 2,5-dimethylfuran, at a rate faster than 0.050 ppm of ozone.

Ozone is a very powerful oxidant, but it reacts with saturated organic compounds, such as those found in Groups I and III, at a very slow rate. For a homogeneous reaction to alter the concentration of indoor pollutants, it must occur at a rate that is comparable to, or faster, than the air exchange rate (29). The smaller the air exchange rate, the more time available for homogeneous chemistry to occur. During the ozone/ETS experiments the chamber was deliberately ventilated at a very small rate (0.018 h⁻¹) to provide conditions that favored ozone reactions with ETS constituents. In typical indoor settings, the air exchange rate is significantly larger than 0.018 h⁻¹ (30), and, consequently, there is less time than in the chamber experiments for ozone to react with the constituents of ETS. In other words, under normally occurring indoor conditions ozone would have even less of an effect on the concentrations of organic compounds in ETS than that shown in Table 1 and Figures 2–4.

**ΣETS Constituents.** As noted in the Experimental Section, in each experiment the total concentration of ETS constituents with volatilities between those of 2-methylbutane and n-hexadecane was monitored using a total ion current (TIC) procedure. However, this measurement fails to measure formaldehyde and acetaldehyde, two potentially important species. Hence, we have added the concentration of the latter two compounds to the TIC measurement and termed the resulting value “ΣETS”. Figure 5 presents results for the ΣETS for each of the cases examined—no ozone, moderate ozone, and high ozone. The plotted values have been normalized by dividing the ΣETS concentration at time = “t” by the ΣETS concentration at time = “0”. In all nine experiments the ΣETS concentration was measured at t = 0 and t = 2.5 h. In six of the nine experiments the ΣETS concentration was measured at t = 5 h. To put Figure 5 in perspective relative to Figures 2–4, the average initial concentration of the ΣETS for the nine experiments was 4260 µg/m³ compared to an initial concentration of 1600 µg/m³ for the sum of the compounds that make up Groups I, II, and III. That is, the compounds in Groups I, II, and III account for 40% of the compounds measured in the ΣETS concentration. In the no ozone experiments, the ΣETS concentration is approximately 95% of its initial value after 2.5 h and 75% of its initial value after 5 h (due to surface losses and air exchange). In the moderate ozone experiments, the ΣETS concentration is approximately 75% of its initial value after 2.5 h and 65% at the 5-h point. In the high ozone experiments, the ΣETS concentration is about 85% of its initial value at 2.5 h and 65% of its initial value at 5 h. Hence, when the changes in ΣETS concentrations in the presence of moderate or high ozone concentrations are compared with those in the presence of no ozone, taking into account the analytical precision, it is apparent that there is little difference among the three scenarios. This is an extension of the results obtained by monitoring the Group I, II, and III constituents of ETS. Ozone only reacts with a subset of the organic compounds that contribute to the ΣETS signal; however, other compounds are generated as a consequence of the reactions with ozone. Furthermore, not all of the products of the ozone/VOC chemistry will contribute to the ΣETS signal. Indeed, if all of the products could be accounted for, one would actually expect the concentration of organic compounds in the chamber air to be greater when ozone is present than when it is absent. This last statement derives from the fact that, in general, the reaction of ozone with an unsaturated organic compound produces more than one product. However, some of these products will wind up in the condensed phase (secondary organic aerosols or absorbed on chamber surfaces). Other products such as certain organic acids, although in the gas phase, are not readily detected by the analytical procedures employed in this study (the analytical methods are more sensitive to nonpolar compounds than to oxidized species (19)).

**Odor.** It is interesting to note that some of the more odorous constituents of ETS are among the compounds that
react with moderate or high levels of ozone. The smell of ETS is a composite, representing the net contribution of numerous odorous compounds. To the extent that the concentrations of some of these compounds are altered by ozone, ozone is expected to alter the smell of ETS. This does not mean that the resulting mixture is less irritating or harmful; it simply has an odor that may be less offensive to some individuals.

**Irritation.** At elevated concentrations, ozone is a known sensory irritant. At settings that result in low ozone concentrations, the ozone generating device has little effect on the concentrations of the organic compounds present in tobacco smoke. At settings that result in high ozone concentrations, the ozone generating device only reduces the concentration of a small subset of the organics present in tobacco smoke—primarily those compounds with unsaturated carbon—carbon bonds. However, the reduction in the concentration of these unsaturated hydrocarbons is countered by an increase in the concentration of a number of more highly oxidized compounds (6, 16, 23). Given their increased water solubility, many of the oxidation products are anticipated to be stronger mucous membrane irritants than their precursors. Indeed, recent experiments using a mouse bioassay support this conjecture (8, 9).

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