

Production of the Hydroxyl Radical in Indoor Air

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Certain alkenes known to have significant indoor concentrations react with O₃ at rates that are comparable to or faster than typical air exchange rates in commercial and residential buildings; these reactions produce the hydroxyl radical (OH) in meaningful yields. The present study uses a one-compartment mass balance model to investigate the indoor production of OH as a consequence of such chemistry. Important sources for indoor OH include the reactions of O₃ with *d*-limonene, α -terpinene, 2-methyl-2-butene, and α -pinene, while important sinks include the reaction of indoor OH with *d*-limonene, nitrogen dioxide, ethanol, formaldehyde, carbon monoxide, and isoprene. The modeling indicates that the OH sources and sinks equilibrate in tens of milliseconds, an interval much shorter than the residence time for a parcel of indoor air. Indoor O₃ drives the production of OH, which scales nonlinearly with the concentration of O₃. At 20 ppb indoor O₃, using average indoor concentrations for key reactants, the model predicts a steady-state indoor OH concentration of 6.7×10^{-6} ppb (1.7×10^5 molecules/cm³). This is smaller than a typical midday outdoor OH concentration of 2×10^{-4} ppb (5×10^6 molecules/cm³) but larger than measured nighttime outdoor levels. The OH radical at 6.7×10^{-6} ppb will oxidize saturated organics 2–5 orders of magnitude faster than O₃ at 20 ppb. In many cases, the expected oxidation products are more irritating and corrosive than their precursors.

Introduction

The hydroxyl radical (OH) has a very low outdoor concentration [typical midday values in the range of 10^6 – 10^7 molecules/cm³ (1)], but its importance is amplified by the fact that it reacts quickly with most trace atmospheric constituents. Indeed, the OH concentration determines the atmospheric lifetimes of many compounds (2), and, consequently, it has been called “mother nature’s vacuum cleaner” (3).

Whereas the concentration of the hydroxyl radical outdoors has been the object of intense research, the concentration of the hydroxyl radical indoors has received

little attention. This reflects the assumption that hydroxyl radicals transported from the outdoors to the indoors are almost immediately scavenged by indoor gas phase species (and, to a much lesser extent, by indoor surfaces). However, this point of view neglects the possibility that indoor chemistry can generate hydroxyl radicals.

In 1992, Paulson et al. (4), Paulson and Seinfeld (5), and Atkinson et al. (6) demonstrated that, under atmospheric conditions, the OH radical is produced from the gas-phase reaction of ozone (O₃) with isoprene, 1-octene, ethene, and a series of monoterpenes. More recent studies (7, 8) have extended the measurements to include over two dozen alkenes. A number of alkenes, including *d*-limonene, α -pinene, and α -terpinene, are known to often have significant indoor concentrations (in the ppb range). Since indoor O₃ concentrations are also frequently significant (see ref 9 and references therein), O₃/alkene reactions appear to be a potentially important source of OH indoors.

In a seminal paper, published prior to the studies just discussed, Nazaroff and Cass (10) modeled chemically reactive pollutants in indoor air. Their overall kinetic mechanism included a generic reaction that could produce OH indoors (olefins and ozone \rightarrow 0.5RCHO + 0.5HCHO + 0.3HO₂ + 0.31RO₂ + 0.14OH + 0.03RO). In Table VI of the Nazaroff and Cass study, a calculated indoor OH concentration of 2.2×10^{-6} ppb is reported for “base case” conditions. However, apart from the listing in this table, the production of indoor OH was not discussed in the paper. More recently Weschler et al. (11, 12) and Tuazon et al. (13) have speculated that certain reactions between species found in indoor air may be significant sources of indoor free radicals, including the hydroxyl radical. In the present study, we examine the specific hypothesis that O₃/alkene reactions are an important source of indoor OH. We have modeled the interactions between the major sources and sinks of OH in a typical indoor setting. Using our best judgment as of this writing, we have included the 13 indoor reactions that produce the most OH (based on reaction rates, reaction yields, and reactant concentrations) and the 39 indoor reactions that consume the most OH (based on reaction rates and reactant concentrations). The relevant rate constants and typical indoor reactant concentrations have been assembled from the literature. The results that follow suggest that conditions conducive to the formation of indoor hydroxyl radicals are more common than have been assumed and that the indoor concentration of OH may sometimes approach outdoor levels.

Indoor Reactant Concentrations

Various alkenes found in indoor air react with O₃ to produce OH. The alkenes that are OH precursors also react with OH once it is formed (i.e., they produce and remove OH). Other species (both organic and inorganic gases and vapors) do not contribute to OH production but rapidly react with OH. The indoor concentrations of these sources and sinks strongly influence the modeled OH concentration.

The indoor concentrations that have been used as the base case in this study are intended to represent average conditions and have been taken from several reports. The majority of the values come from a 1994 literature survey of indoor volatile organic compounds (VOCs) by Brown et

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al. (14). For a given VOC, this survey summarizes the indoor geometric mean concentrations from multiple studies as a "weighted average" of geometric means (WAGM); see ref 14 for details. For a few reactants, the values have been taken from a national VOC data base assembled by Shah and Singh (15).

Compounds with five carbons or less are often referred to as very volatile organic compounds (VVOCs). The sorption methods that are normally used to sample indoor VOCs are not suited to sampling VVOCs, and consequently, there are few published measurements of indoor VVOC concentrations. Most of the indoor VVOC concentrations adopted for use in this study are simply outdoor concentrations taken from a carefully scrutinized data set for an urban site in the southern United States (see Table 7 in ref 16), supplemented by values reported in a book by Graedel (3). Even if VVOCs have no indoor sources, their indoor concentrations are expected to be comparable to or only slightly lower than their outdoor levels. This is a consequence of outdoor-to-indoor transport coupled with the fact that removal of VVOCs by indoor surfaces is small. In the case of one VVOC, isoprene, the concentration has been estimated using a different approach since it is a major body effluent. A human at rest is reported to emit isoprene at a rate of approximately 350 $\mu\text{g}/\text{h}$ (17). If one assumes an occupant density of 1 person/60 m^3 and an air exchange rate of 1.0 air change/h (ach), the resultant steady-state concentration is 2 ppb.

The values for indoor nitrogen dioxide (NO_2) and carbon monoxide (CO) are based on our own measurements (ref 12 and unpublished results) as well as measurements in over 50 California homes (18). The values for ammonia (NH_3) and sulfur dioxide (SO_2) are adopted from measurements by Brauer et al. (19) in Massachusetts homes. The reader should note that nitric oxide (NO) is not among the compounds that are listed as important indoor sinks for OH. The current report focuses on periods with elevated O_3 concentrations. Our studies (12) have demonstrated that when indoor O_3 concentrations are high (>10 ppb), indoor NO concentrations are low (<1 ppb). This reflects the fact that O_3 and NO react at a very fast rate [$4.4 \times 10^{-4} \text{ ppb}^{-1} \text{ s}^{-1}$ at 25 $^\circ\text{C}$ (20)]. The measured amount of indoor O_3 is a net concentration; it is the concentration that remains after any NO accumulated indoors or introduced from outdoors has been titrated.

Given the importance of certain alkenes to the hypothesis under examination, a brief review of their indoor sources is warranted. *d*-Limonene and α -terpinene are monoterpenes that tend to co-occur in nature, have similar boiling points (176.5 and 175 $^\circ\text{C}$, respectively), and are often not distilled from one another. Commercial "dipentene" contains both of these species (somewhat confusing, since this term also refers to the racemic mixture of *d*- and *l*-limonene). Dipentene is used in large amounts as a solvent for paints, varnishes, and enamels that contain synthetic resins; it's also used as an anti-skinning agent and a wetting agent in the dispersion of pigments; finally, since it is a good solvent for rubber, it is used in the processing of both natural and synthetic rubber. Pine oil is another major source of both *d*-limonene and α -terpinene. Pine oil is used in cleaners and disinfectants (e.g., Pine-Sol); it is also sometimes used in the manufacture of glues and adhesives. Yearly production of pine oil is approximately 20 000 t (21). In both dipentene and pine oil there tends to be significantly more *d*-limonene than

α -terpinene, but the ratio varies with the initial source (Southeastern pine stumps, fractionation of crude sulfate turpentine, etc.). α -Pinene is the major constituent of oil of turpentine (21). Terpenes such as *d*-limonene, α -terpinene, α -pinene, and camphene are used in fragrance formulations incorporated in personal care products and other household consumables (22, 23). Terpenes also are emitted from wood products, including flooring, paneling, and furniture (23). Styrene has numerous indoor sources, including smoking (24), carpets (25), and adhesives (23). As noted above, isoprene is a major body effluent (17) and also is emitted by house plants and other vegetation (3). The most common sources for the other VVOCs included in the modeling are motor vehicles and combustion processes (smoking, cooking, heating, etc.) (3).

Of the terpenes, *d*-limonene is the most frequently detected indoors, followed by α -pinene (14, 15, 22–24). The reported WAGM for *d*-limonene is 3.8 ppb based on measurements in 584 buildings (14). The reported WAGM for camphene is 2.5 ppb, while the reported WAGMs for α -terpinene and α -pinene lie in the range between 0.2 and 0.9 ppb (14).

In the case of certain alkenes, the indoor concentrations are significantly affected by O_3 . It is unclear from the literature whether reported VOC concentrations were measured in the absence or presence of O_3 . We have adopted the conservative assumption that the reported concentrations have been measured in the absence of O_3 . In our model calculations, we have adjusted these concentrations downward (assuming 1 ach, 20 ppb O_3 , and applying the rate constant for the relevant O_3 /alkene reaction). This correction is largest for the alkenes that react fastest with O_3 (i.e., α -terpinene, 2-methyl-2-butene, and *d*-limonene) and becomes less significant as the O_3 /alkene rate constant becomes smaller. Nonetheless, the correction has been applied to the indoor concentrations of all VOCs that react with O_3 at a rate faster than $1 \times 10^{-8} \text{ ppb}^{-1} \text{ s}^{-1}$.

Sources for OH Indoors: Ozone/Alkene Reactions

Table 1 shows calculated OH production rates for a typical indoor environment with an elevated O_3 concentration (20 ppb). It has been constructed around the 13 indoor alkenes that we hypothesize to be responsible for the largest production rates of hydroxyl radicals. An alkene with a large indoor concentration will not be an important OH precursor if it reacts slowly with O_3 (i.e., indoor air can have an elevated O_3 concentration and a large total VOC concentration but a low OH-producing capacity if the VOCs are relatively unreactive with O_3). In addition to the calculated OH production rates, Table 1 shows the values from which these rates have been derived. For each O_3 /alkene reaction, this includes the OH yield, the rate constant, and an average indoor alkene concentration (see Indoor Reactant Concentrations).

OH Yields. The production of OH from the reaction of O_3 with an alkene is a multistep process whose chemistry has been detailed in a recent paper by Atkinson et al. (8). In brief, the initial product of the O_3 /alkene reaction is an ozonide that rapidly decomposes into one of two possible combinations of a carbonyl and a biradical. The energy-rich biradical then rearranges or reacts via a number of different pathways. Two of the possible pathways, the ester channel and the hydroperoxide channel, lead to the formation of OH. The "OH formation yield" describes the

TABLE 1

Calculated Production Rates for Hydroxyl Radical within Typical Indoor Environment Assuming Indoor O₃ Concentration of 20 ppb
$$\text{O}_3 + \text{alkene} \rightarrow \text{intermediates} \rightarrow \text{OH} + \text{other products}$$

$$d[\text{OH}]/dt = (\text{yield})k[\text{alkene}][\text{O}_3]$$

alkene	typical indoor concn (ppb)		OH yield	rate constant (O ₃ +alkene) (ppb ⁻¹ s ⁻¹)	calcd OH production rate (ppb s ⁻¹)
	no O ₃ ^a	20 ppb O ₃ ^b			
<i>d</i> -limonene	4 ^c	2.9	0.86	5.1 × 10 ⁻⁶ <i>h</i>	2.6 × 10 ⁻⁴
α-terpinene	0.5 ^c	0.03	0.91	2.1 × 10 ⁻⁴ <i>h</i>	1.2 × 10 ⁻⁴
2-methyl-2-butene	0.4 ^d	0.23	0.89	1.0 × 10 ⁻⁵ <i>i</i>	4.2 × 10 ⁻⁵
α-pinene	0.5 ^c	0.43	0.85	2.1 × 10 ⁻⁶ <i>h</i>	1.6 × 10 ⁻⁵
<i>trans</i> -2-butene	0.3 ^d	0.22	0.64	5.3 × 10 ⁻⁶ <i>i</i>	1.5 × 10 ⁻⁵
<i>cis</i> -2-butene	0.3 ^d	0.24	0.41	3.2 × 10 ⁻⁶ <i>i</i>	6.4 × 10 ⁻⁶
isoprene	2 ^e	2	0.27	3.0 × 10 ⁻⁷ <i>i</i>	3.2 × 10 ⁻⁶
isobutene	0.5 ^d	0.49	0.84	2.8 × 10 ⁻⁷ <i>i</i>	2.3 × 10 ⁻⁶
styrene	0.5 ^c	0.49	0.37	4.2 × 10 ⁻⁷ <i>j</i>	1.5 × 10 ⁻⁶
propene	0.5 ^d	0.49	0.33	2.9 × 10 ⁻⁷ <i>k</i>	9.4 × 10 ⁻⁷
camphene	2.5 ^c	2.5	0.15	2.2 × 10 ⁻⁸ <i>l</i>	1.7 × 10 ⁻⁷
ethene	1.5 ^d	1.5	0.12	4.3 × 10 ⁻⁸ <i>k</i>	1.5 × 10 ⁻⁷
1,3-butadiene	0.3 ^f	0.3	0.08	2.0 × 10 ⁻⁷ <i>m</i>	9.5 × 10 ⁻⁸
air exchange (i.e., E _x [OH] _{otdr})	[OH] _{otdr} ^g = 2.0 × 10 ⁻⁴			E _x = 2.8 × 10 ⁻⁴ s ⁻¹	5.6 × 10 ⁻⁸

^a Average VOC concentration in the absence of O₃. ^b VOC concentration in the presence of 20 ppb O₃. ^c Ref 14. ^d Derived from outdoor concentrations (16). See discussion in text. ^e Based on human emissions (17). See discussion in text. ^f Ref 15. ^g Ref 1. ^h Ref 26. ⁱ Ref 27. ^j Ref 13. ^k Ref 20. ^l Ref 28. ^m Ref 29.

amount of OH produced when 1 molecule of O₃ reacts with 1 molecule of a given alkene.

The second column in Table 1 lists the expected hydroxyl yields for the O₃/alkene reactions in question. Most of these yields are based on recent measurements (7). However, measured yields have not been reported for α-terpinene and styrene; in these cases, the yields have been estimated using an approach recommended by Atkinson and Aschmann (7). In general, the greater the number of substituent groups, the greater the OH yield. The structure of α-terpinene matches an alkyl-substituted ethene of the type R₁R₂C=CHR₃, for which a yield of 0.91 has been suggested; the structure of styrene matches the type RCH=CH₂, for which a yield of 0.37 has been suggested. The measured OH formation yields are highest for *d*-limonene, α-pinene, 2-methyl-2-butene, and isobutene (0.84–0.89) and lowest for 1,3-butadiene, ethene, and camphene (0.08–0.15).

Rate Constants. The rate constants listed in Table 1 for the various O₃/alkene reactions have been taken primarily from recent measurements or critical summaries by Atkinson and co-workers (13, 20, 26–29). The fastest reaction is that between O₃ and α-terpinene (2.1 × 10⁻⁴ ppb⁻¹ s⁻¹), followed by the reactions of O₃ with 2-methyl-2-butene, *trans*-2-butene, *d*-limonene, *cis*-2-butene, and α-pinene (1.0 × 10⁻⁵ to 2.1 × 10⁻⁶ ppb⁻¹ s⁻¹).

Indoor Ozone Concentrations. In Table 1, the indoor chemistry that produces the hydroxyl radical is driven by ozone. The most important source of indoor ozone is outdoor-to-indoor transport. Two decades ago, Shair and colleagues at California Institute of Technology as well as Thompson and co-workers at University of California, Riverside, demonstrated that indoor O₃ concentrations were sometimes a significant fraction of outdoor levels (30–33). Numerous investigators have confirmed their findings (ref 9 and references therein). The ratio of indoor-to-outdoor O₃ concentrations (I/O) is a function of the air exchange rate and the rate of O₃ removal by surfaces (9). Indoor O₃ concentrations typically range from 20–30% of outdoor

levels in moderately ventilated office space to 50–70% of outdoor levels in highly ventilated classrooms, conference rooms, and dining areas (see Tables I and III in ref 9). A recent study conducted at a classroom in southwest Mexico City reported a median indoor O₃ concentration of 113 ppb (*n* = 27, median outdoor value = 191 ppb) with the windows and doors open and 27 ppb (*n* = 41, median outdoor value = 143 ppb) with the windows and doors closed (34). At a commercial building in Burbank, CA, the 95th percentile concentration of indoor O₃ was 56 ppb during the month of September, and during those months when the outdoor O₃ concentrations were at their lowest, the 95th percentile concentrations for indoor O₃ were still greater than 5 ppb (11.4 ppb, November; 7.3 ppb, December; and 18.4 ppb, January; see Table 1 in ref 12). At an office/lab complex in Red Bank, NJ, during the summer of 1988, there were more than 50 days that indoor O₃ levels exceeded 40 ppb (9). During winter months, indoor O₃ concentrations were frequently above 4 ppb at this site.

The salient point is that indoor O₃ concentrations can be a significant fraction of outdoor concentrations; during the summer in urban areas, indoor levels greater than 50 ppb are not unusual, and even during the winter in northern climates, indoor O₃ levels of several ppb are common. In the current study, the base case indoor O₃ concentration is 20 ppb.

OH Production Rates. The final column in Table 1 presents the OH production rate, calculated using the values in the preceding three columns and a value of 20 ppb for indoor O₃. The entries have been listed in decreasing order of production rate (given the representative indoor concentrations, corrected for the presence of O₃). For the conditions presented, the indoor reaction between O₃ and *d*-limonene produces indoor hydroxyl at the fastest rate, followed by the reactions of O₃ with α-terpinene, 2-methyl-2-butene, and α-pinene. Although representative values were chosen (see Indoor Reactant Concentrations), the rank ordering could change if different values were substituted for the indoor concentrations of the alkenes.

TABLE 2

Calculated Rate Constants for Removal of Hydroxyl Radical within Typical Indoor Environment

$$\text{OH}_{\text{indr}} + \text{reactant} \rightarrow \text{products}$$

$$-d[\text{OH}]/dt = k[\text{reactant}][\text{OH}_{\text{indr}}]$$

reactant	rate constant ($\text{OH}_{\text{indr}} + \text{reactant}$) ($\text{ppb}^{-1} \text{s}^{-1}$)	typical indoor concn (ppb)		calcd rate constant for OH removal (s^{-1})
		no O_3^j	20 ppb O_3^k	
<i>d</i> -limonene	4.2 ^a	4 ^l	2.9	12.3
nitrogen dioxide	0.30 ^{b,c}	30 ^m	30 ^m	9.0
ethanol	0.079 ^b	100 ^l	100 ^l	7.9
formaldehyde	0.24 ^b	30 ⁿ	30 ⁿ	7.2
carbon monoxide	0.0059 ^b	1000 ^m	1000 ^m	5.9
isoprene	2.5 ^d	2 ^o	2	5.0
camphene	1.3 ^e	2.5 ^l	2.5	3.2
acetaldehyde	0.39 ^b	5 ⁿ	5 ⁿ	2.0
1,2,4-trimethylbenzene	0.81 ^f	2 ^l	2 ^l	1.6
toluene	0.15 ^g	10 ^l	10 ^l	1.5
1,3,5-trimethylbenzene	1.4 ^f	1 ^l	1 ^l	1.4
<i>m</i> -xylene	0.62 ^g	2 ^l	2 ^l	1.2
<i>o</i> -xylene	0.37 ^g	3 ^l	3 ^l	1.1
styrene	1.5 ^h	0.5 ^l	0.49	0.74
<i>p</i> -xylene	0.37 ^g	2 ^l	2 ^l	0.74
isobutene	1.3 ^g	0.5 ^p	0.49	0.64
α -pinene	1.4 ^a	0.5 ^l	0.43	0.60
benzaldehyde	0.32 ^g	1.6 ⁿ	1.6 ⁿ	0.51
1,3-butadiene	1.65 ^g	0.3 ⁿ	0.3	0.50
2-methyl-2-butene	2.1 ^d	0.4 ^p	0.23	0.48
ethylbenzene	0.185 ^g	2 ^l	2 ^l	0.37
<i>trans</i> -2-butene	1.6 ^g	0.3 ^p	0.22	0.35
<i>cis</i> -2-butene	1.4 ^g	0.3 ^p	0.24	0.34
methane	0.00017 ^b	2000 ^q	2000 ^q	0.34
ethene	0.21 ^{b,c}	1.5 ^p	1.5	0.32
propene	0.64 ^{b,c}	0.5 ^p	0.49	0.31
<i>n</i> -undecane	0.295 ^l	1 ^l	1 ^l	0.30
α -terpinene	8.9 ^a	0.5 ^l	0.03	0.27
<i>n</i> -butane	0.063 ^l	4 ^p	4 ^p	0.25
methanol	0.023 ^b	10 ^l	10 ^l	0.23
<i>n</i> -pentane	0.10 ^l	2 ^p	2 ^p	0.20
benzene	0.032 ^g	5 ^l	5 ^l	0.16
acetone	0.0057 ^b	10 ^l	10 ^l	0.057
propane	0.027 ^b	1.5 ^p	1.5 ^p	0.041
ammonia	0.0039 ^b	10 ^r	10 ^r	0.039
ozone	0.0017 ^b	20 ^s	20 ^s	0.034
sulfur dioxide	0.022 ^{b,c}	1 ^r	1 ^r	0.022
ethane	0.0062 ^b	2.5 ^p	2.5 ^p	0.016
1,1,1-trichloroethane	0.00023 ^b	10 ^l	10 ^l	0.002
surface removal ($k_d(A/V)$)	$k_d = 7 \times 10^{-4} \text{ m s}^{-1}$	$A/V = 2.8 \text{ m}^{-1}$		0.002
air exchange (E_x)	$E_x = 2.8 \times 10^{-4} \text{ s}^{-1}$			0.00028

^a Ref 35. ^b Ref 20. ^c This reaction is in the falloff region between third and second order. The tabulated value is the effective bimolecular rate constant for 1 atm and 25 °C. ^d Ref 36. ^e Ref 28. ^f Ref 37. ^g Ref 38. ^h Ref 39. ⁱ Ref 40. ^j Average VOC concentration in the absence of ozone. ^k VOC concentration in the presence of 20 ppb O_3 . ^l Ref 14. ^m Ref 18. ⁿ Ref 15. ^o Based on human emissions (17). See discussion in text. ^p Derived from outdoor concentrations (16). See discussion in text. ^q Derived from outdoor concentrations (3). See discussion in text. ^r Ref 19. ^s See discussion in text titled Indoor Ozone Concentrations.

For comparison with the O_3 /alkene reactions, the last row of Table 1 addresses the transport of outdoor hydroxyl radical (OH_{otdr}) to the indoors. Given a rate of air exchange, E_x , between the outdoors and indoors of $2.8 \times 10^{-4} \text{ s}^{-1}$ (this is equivalent to 1 air change/h) and a concentration of $2.0 \times 10^{-4} \text{ ppb}$ ($5 \times 10^6 \text{ molecules/cm}^3$) for OH_{otdr} (*I*), transport results in an indoor OH production rate of $5.6 \times 10^{-8} \text{ ppb s}^{-1}$. Compared with the production rates that result from the reaction of ozone with the tabulated alkenes, outdoor-to-indoor transport is a negligible source.

In addition to the O_3 /alkene reactions and outdoor-to-indoor transport, other potential sources of indoor OH include the reaction between HO_2 and NO and the photolysis of O_3 ($\lambda < 320 \text{ nm}$), HONO ($\lambda < 400 \text{ nm}$), and H_2O_2 ($\lambda < 360 \text{ nm}$) (2). The analysis presented by Nazaroff and Cass (10) suggests that the OH production rates as a

consequence of these processes are normally less than those resulting from the faster O_3 /alkene reactions. Hence, the focus of this report is the latter set of reactions.

Sinks for OH Indoors: OH Reactions with Organic/Inorganic Compounds

As noted in the Introduction, the hydroxyl radical reacts rapidly with many airborne pollutants. Table 2 addresses the removal of OH as a consequence of its reactions with various organic and inorganic compounds commonly found in indoor air. The compounds listed in Table 2 are those that react with OH most rapidly. (Although other VOCs are commonly found indoors, a VOC with a large concentration will not be an important sink if it reacts slowly with OH; such compounds are not included in the table.) For each compound, Table 2 lists the reported (20, 28, 35–40) second-

order rate constant for reaction with OH, its typical indoor concentration in the presence of 20 ppb O₃, and the resulting pseudo-first-order rate constant for OH removal (the product of the second-order rate constant and the reactant concentration). Since the concentrations of these reactants are many orders of magnitude greater than that of indoor OH, the concentrations of the reactants, to a first approximation, do not change significantly as a consequence of their reaction with OH.

OH Removal Rates. The calculated pseudo-first-order rate constants for OH removal are rank listed in Table 2 (highest to lowest). Given the tabulated reactant concentrations, the six most significant sinks for indoor OH are *d*-limonene (12.3 s⁻¹), nitrogen dioxide (9.0 s⁻¹), ethanol (7.9 s⁻¹), formaldehyde (7.2 s⁻¹), carbon monoxide (5.9 s⁻¹), and isoprene (5.0 s⁻¹).

The last two entries in Table 2 are "sinks" that do not involve homogeneous chemistry: removal by indoor surfaces (0.002 s⁻¹) and air exchange (0.00028 s⁻¹). The removal of OH by indoor surfaces depends on its deposition velocity (*k_d*) and the surface-to-volume ratio (*A/V*) within the space. Assuming that near surface air flow is determined by natural convection, we have used a transport-limited deposition velocity of 0.0007 m s⁻¹ (10, 41). Based on the studies of Mueller et al. (42), we have assumed a value of 2.8 m⁻¹ for *A/V*. In the case of air exchange, the tabulated rate constant is simply the rate at which indoor air is exchanged with outdoor air. It is apparent that these two sinks, deposition and air exchange, are of negligible importance compared to reactions with indoor gas phase species.

A final point regarding Table 2 is that some of the same alkenes that play a major role in hydroxyl removal also play a major role in hydroxyl formation. These include *d*-limonene, isoprene, α -terpinene, camphene, styrene, α -pinene, 2-methyl-2-butene, and the butene isomers. As a consequence, the indoor hydroxyl radical concentration is less sensitive to the concentrations of these alkenes than it would be if they were only "sources" (see Sensitivity of Indoor OH to Selected Parameters).

Mathematical Modeling

To estimate indoor hydroxyl radical concentrations, the sources and sinks presented in Tables 1 and 2 can be incorporated in a simple one-compartment mass balance model. The compartment represents an indoor environment surrounded by the outdoors; species can be transported into or out of the compartment. Within the compartment, the rate of change of the hydroxyl radical concentration is described by

$$d[\text{OH}_{\text{indr}}]/dt = E_x[\text{OH}_{\text{otdr}}] + \sum y_i k_{O_3i} [\text{O}_3][\text{VOC}_i] - E_x[\text{OH}_{\text{indr}}] - k_d(A/V)[\text{OH}_{\text{indr}}] - \sum k_{\text{OH}_i}[\text{OH}_{\text{indr}}][\text{VOC}_i] \quad (1)$$

where [OH_{indr}] is the indoor hydroxyl radical concentration (ppb); *E_x* is the rate at which air is exchanged with outdoors (s⁻¹); [OH_{otdr}] is the outdoor hydroxyl radical concentration (ppb); *y_i* is the yield of the *i*th O₃/alkene reaction (see Table 1); *k_{O₃i}* is the second-order rate constant for the *i*th O₃/alkene reaction (ppb⁻¹ s⁻¹, see Table 1); [O₃] is the indoor ozone concentration (ppb); [VOC_{*i*}] is the indoor concentration of the *i*th VOC (ppb); *k_d* is the indoor deposition velocity for the hydroxyl radical (m s⁻¹); *A/V* is the surface-

to-volume ratio within the indoor environment (m⁻¹); and *k_{OH_i}* is the second-order rate constant for the *i*th OH/VOC reaction (ppb⁻¹ s⁻¹, see Table 2).

As noted above (see Indoor Reactant Concentrations), we have adopted the conservative assumption that the alkene concentrations reported in the literature have been measured in the absence of O₃. In all of our model calculations, we have reduced these concentrations to account for losses due to reaction with ozone (assuming constant emission and air exchange rates):

$$[\text{VOC}_i] = [\text{VOC}_{i0}](E_x/(E_x + k_{O_3i}[\text{O}_3])) \quad (2)$$

where [VOC_{*i*0}] is the indoor concentration of the *i*th VOC (ppb) in the absence of ozone.

If the sources and sinks are constant (a reasonable approximation for the time scales of interest), steady-state is established with a characteristic time of

$$1/(E_x + k_d(A/V) + \sum k_{\text{OH}_i}[\text{VOC}_i]) \quad (3)$$

This is simply the reciprocal of the sum of the values from the last column in Table 2 and is approximately 0.015 s. Hence, steady-state is established in a time interval much shorter than the residence time for a parcel of indoor air. Under steady-state conditions

$$[\text{OH}_{\text{indr}}] = (E_x[\text{OH}_{\text{otdr}}] + \sum y_i k_{O_3i} [\text{O}_3][\text{VOC}_i]) / (E_x + k_d(A/V) + \sum k_{\text{OH}_i}[\text{VOC}_i]) \quad (4)$$

For the conditions presented in Tables 1 and 2, the model yields an indoor hydroxyl radical concentration of 6.7 × 10⁻⁶ ppb. This is smaller than a typical outdoor midday OH concentration of 2 × 10⁻⁴ ppb (5 × 10⁶ molecules/cm³) but is at least 4 times larger than typical outdoor nighttime values measured by Tanner and Eisele (1). As an additional comparison, Goldstein et al. (43) have reported a winter mean outdoor OH concentration at northern midlatitudes of 6 × 10⁻⁶ ppb (1.4 × 10⁵ molecules/cm³).

Sensitivity of Indoor OH to Selected Parameters

How sensitive is the calculated concentration of indoor OH to the indoor concentrations of key alkenes, as well as O₃? The matrix presented in Table 3 partially addresses this question. It includes nine alkenes that are anticipated to be among those most important to the indoor formation of OH through reaction with O₃ (see Table 1). Scenario 1 uses the base case concentrations presented in Tables 1 and 2. In each of the subsequent scenarios, 2–11, the concentrations of the key alkenes or O₃ are altered from the base case while the concentrations of all other species in the overall kinetic mechanism remain unchanged from those listed in Tables 1 and 2. (Note that in each scenario the tabulated alkene concentrations reflect, through the application of eq 2, any losses due to reaction with O₃.) The final row of Table 3 contains the resulting indoor hydroxyl concentrations, calculated using eq 4. The following paragraphs discuss the various scenarios in greater detail.

In scenario 2 of Table 3, the indoor concentration of O₃ remains at 20 ppb, but the indoor concentrations of each of the alkenes is one-tenth the value used in the base case. The resulting indoor hydroxyl concentration is ~one-seventh the base case (0.92 × 10⁻⁶ ppb). The fact that the relative reduction in hydroxyl radical concentration is less

TABLE 3

Indoor Hydroxyl Radical Concentrations for Various Scenarios^a

	1 base case	2 1/10 [VOC] base case	3 3 times [VOC] base case	4 no VOC	5 only limonene	6 only terpinene	7 only 2-methyl-2-butene	8 only pinene	9 low ozone	10 no ozone	11 no alkenes
ozone	20	20	20	20	20	20	20	20	1	0	20
<i>d</i> -limonene	2.9	0.29	8.7	2.9	2.9	0	0	0	3.9	4	0
α -terpinene	0.03	0.003	0.09	0.03	0	0.03	0	0	0.28	0.5	0
2-methyl-2-butene	0.23	0.023	0.69	0	0	0	0.23	0	0.39	0.4	0
α -pinene	0.43	0.043	1.3	0.43	0	0	0	0	0.5	0.5	0
<i>trans</i> -2-butene	0.22	0.022	0.66	0	0	0	0	0	0.29	0.3	0
<i>cis</i> -2-butene	0.24	0.024	0.72	0	0	0	0	0	0.3	0.3	0
isoprene	2	0.2	6	0	0	0	0	0	2	2	0
isobutene	0.49	0.049	1.5	0	0	0	0	0	0.5	0.5	0
styrene	0.49	0.049	1.5	0.49	0	0	0	0	0.5	0.5	0
hydroxyl _{indr} ^b	6.7×10^{-6}	0.92×10^{-6}	12.5×10^{-6}	6.3×10^{-6}	4.2×10^{-6}	2.5×10^{-6}	0.89×10^{-6}	0.32×10^{-6}	1.0×10^{-6}	0.0007×10^{-6}	0.0012×10^{-6}

^a All concentrations are in ppb. ^b For each scenario, the outdoor hydroxyl radical concentration is 2.0×10^{-4} ppb (5×10^6 molecules/cm³).

than the relative reductions in VOC concentrations reflects the fact that these alkenes are sinks as well as sources; although the overall rate at which OH is produced has been significantly reduced, the rate at which OH is consumed has also been reduced. This result also illustrates that the overall OH production mechanism is nonlinear with respect to VOC concentrations.

The base case alkene concentrations are average values. However, these concentrations can be significantly larger in highly polluted indoor environments. In scenario 3, the indoor concentration of O₃ is again 20 ppb, but the indoor concentrations of each of the alkenes is three times larger than the value used in the base case. The resulting indoor hydroxyl concentration is 1.25×10^{-5} ppb, about twice that of the base case.

In scenario 4, the concentrations of the low molecular weight alkenes (the VVOCs) are assumed to be zero, while the other alkenes remain at their base case concentrations. The reader is reminded that the concentrations of the VVOCs in Table 1 are derived from outdoor concentrations, since there have been few reported indoor measurements of these compounds. This scenario allows us to estimate the impact on indoor OH levels if VVOCs were not present indoors (unlikely). The resulting value for [OH_{indr}], 6.3×10^{-6} ppb, is close to the base case value. This indicates that, when terpenes are present at base case concentrations, the VVOCs have little effect on indoor OH concentrations.

Under base case conditions, *d*-limonene accounts for 56% of indoor OH production, α -terpinene accounts for 26%, 2-methyl-2-butene accounts for 9%, and α -pinene accounts for 3.4%. Together, these four alkenes are responsible for 94% of the indoor OH. If there were no alkenes present indoors other than *d*-limonene (at 2.93 ppb in the presence of 20 ppb O₃), then the resultant indoor OH concentration would be 4.2×10^{-6} ppb (scenario 5). Analogously, if α -terpinene were the only alkene present, the resultant indoor OH concentration would be 2.5×10^{-6} ppb (scenario 6); 2-methyl-2-butene, 0.89×10^{-6} ppb (scenario 7); and α -pinene, 0.32×10^{-6} ppb (scenario 8). Even in the last case, the concentration of indoor OH is 300 times larger than if no indoor chemistry occurred (compare with scenarios 10 and 11).

In scenario 9, each of the alkenes is present at its base case concentration, but the indoor concentration of O₃ is 1 ppb rather than 20 ppb. The resulting value for [OH_{indr}] is 1.0×10^{-6} ppb. Even during winter months in the northeast, indoor O₃ concentrations on the order of 1 ppb are common (this statement is based on our own unpublished measurements). Such concentrations appear to be sufficient to produce indoor hydroxyl concentrations that are comparable to those outdoors at night, provided the appropriate alkenes are present.

The final two columns in Table 3 (10 and 11) present scenarios in which either the indoor ozone concentration is zero or the concentration of each of the key alkenes is zero. In these two scenarios, where the only source of indoor OH is outdoor-to-indoor transport, the calculated concentration of indoor OH is very small (7.1×10^{-10} or 12×10^{-10} ppb, equivalent to 17.5 or 29.5 molecules/cm³). The value for [OH_{indr}] is smaller in the scenario with no O₃ than in that with no alkenes, since in the former situation the OH/alkene reactions remain important sinks.

Figure 1 further examines the sensitivity of indoor OH concentrations to varying concentrations of a given alkene (at 20 ppb O₃). Whereas in scenarios #5–8 the only alkene

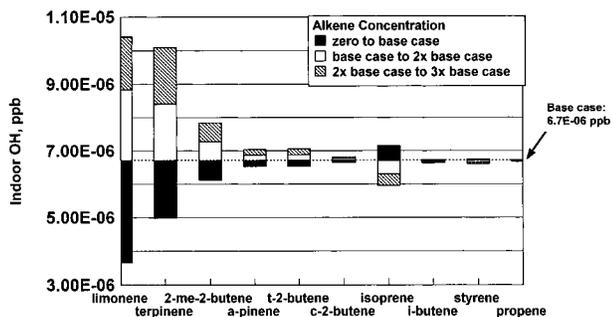


FIGURE 1. Sensitivity of indoor OH concentration to concentration of a given alkene (at 20 ppb ozone). The displayed concentrations (shaded columns) of a given alkene vary from zero to three times the alkene's base case level. The concentrations of all other species remain at their base case levels (see Tables 1 and 2).

present was *d*-limonene, α -terpinene, 2-methyl-2-butene, or α -pinene, respectively, in Figure 1 the concentration of a given alkene is varied while the other alkenes are present at their base case concentrations. There are 10 columns in Figure 1, each representing a concentration range for a given alkene. The columns are shaded to distinguish three different regions: the black region corresponds to an alkene concentration between 0 and base case; the white region corresponds to an alkene concentration between base case and twice base case; and the hatched region corresponds to an alkene concentration between twice and three times base case. Using *d*-limonene as an example and recognizing that its concentration is changing against a backdrop of base case concentrations for all other species, then the following occurs: when it is absent from the indoor environment, the calculated indoor OH level is 3.7×10^{-6} ppb (the bottom of the *d*-limonene column in Figure 1); when its indoor concentration is twice its base case concentration, the calculated indoor OH is 8.8×10^{-6} ppb (the top of the white segment in the *d*-limonene column); finally, when it is present at three times its base case concentration, the calculated indoor OH is 10.4×10^{-6} ppb (the top of the *d*-limonene column). In other words, the columns in Figure 1 illustrate the manner in which the amount of indoor OH varies as the concentration of a given alkene changes. With all other species at base case concentrations, the OH level is most sensitive to changes in the concentration of *d*-limonene, α -terpinene, and, to a lesser extent, 2-methyl-2-butene. It is interesting to note that, in the case of isoprene, the OH level actually decreases as isoprene's concentration increases, indicating that isoprene is a larger sink than source for the conditions presented in Tables 1 and 2.

In Table 3, scenario 9, the indoor O_3 level was reduced a factor of 20, but the OH level only declined by a factor of 7. This reflects the fact that the smaller O_3 concentration resulted in larger alkene concentrations (see eq 2), and the latter was partially offset by the former. Figure 2 provides a more detailed examination of the nonlinear relationship between indoor O_3 concentrations, plotted on the *x*-axis, and indoor OH concentrations, plotted on the *y*-axis. The indoor O_3 levels are varied from 0 to 200 ppb, while the concentrations of all other species match the values in Tables 1 and 2. The plot shows that indoor OH levels are most sensitive to O_3 at lower indoor O_3 concentrations (<10 ppb O_3). As the O_3 concentration increases, comparable increases in the O_3 concentration produce proportionately smaller increases in OH levels.

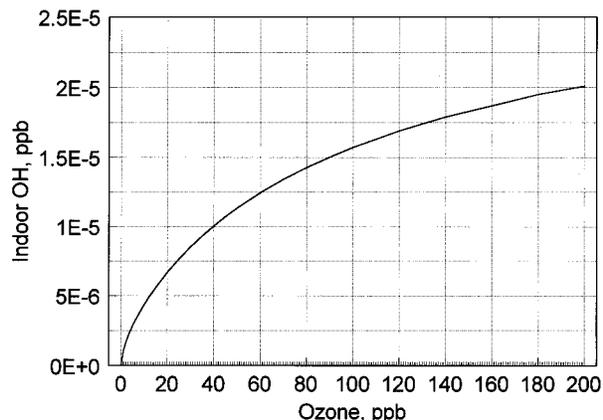


FIGURE 2. Indoor OH concentration as a function of indoor ozone concentration. The concentrations of all other species remain at their base case levels (see Tables 1 and 2).

While discussing the sensitivity of $[OH_{\text{indr}}]$ to the concentrations of key reactants, two sinks merit special comment. One is NO_2 and the other is CO. Given the concentrations in Table 2, NO_2 is the second largest sink for indoor OH, while CO is the fifth largest sink. Although 30 ppb is a reasonable value for indoor NO_2 , we have measured indoor NO_2 concentrations as high as 100 ppb (12). Under these conditions (100 ppb NO_2), the calculated indoor OH concentration is 5.1×10^{-6} ppb (~75% base case). In a similar vein, we have measured indoor CO concentrations as high as 9000 ppb, and under these conditions the calculated indoor OH concentration is 4.0×10^{-6} ppb (~60% base case).

In eq 4, if one compares the term $E_x[OH_{\text{indr}}]$ to the other much larger source terms and compares the term E_x to the other much larger sink terms, the effect of the air exchange rate on the indoor hydroxyl radical concentration appears to be negligible. However, the air exchange rate influences the indoor concentrations of both O_3 and VOCs, key parameters in eq 4. In typical indoor environments, the majority of the indoor O_3 originates outdoors; the larger the air exchange rate, the larger the indoor O_3 concentration resulting in larger indoor OH production rates. Conversely, many VOCs have dominant indoor sources, and the larger the air exchange rate, the smaller their indoor concentrations. If the VOC is primarily a sink (e.g., the saturated organics in Table 2), a smaller indoor VOC concentration means a smaller removal rate for indoor OH. If the VOC is both a source and a sink (e.g., the alkenes that appear in both Tables 1 and 2), the net effect depends on the rates of the O_3 /alkene and OH/alkene reactions. Detailed modeling of the effect of the air exchange rate on indoor OH levels requires estimations of the outdoor concentrations and the indoor emission rates for each of the species in Table 2. The salient point is that changes in the air exchange rate can produce changes in the indoor OH level, but these changes are not simple to predict.

Implications

The reactions between O_3 and most saturated organic compounds are thermodynamically favorable, but kinetically limited. For example, the second-order rate constants for O_3 /alkane reactions are less than 10^{-23} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (2.5×10^{-13} $\text{ppb}^{-1} \text{s}^{-1}$) and those for O_3 /monocyclic aromatics are less than 10^{-20} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (2.5×10^{-10} $\text{ppb}^{-1} \text{s}^{-1}$) (2). At 20 ppb O_3 , the pseudo first-order

rate constants ($k \times [\text{O}_3]$) for these reactions are less than $5 \times 10^{-12} \text{ s}^{-1}$ (alkanes) and $5 \times 10^{-9} \text{ s}^{-1}$ (aromatics). Given typical air exchange rates of 0.7×10^{-4} to $5.6 \times 10^{-4} \text{ s}^{-1}$, the reactions of saturated organics with O_3 are too slow to be significant indoors. On the other hand, reactions between OH and most organic compounds are both thermodynamically and kinetically favorable [second-order rate constants in the range of 5×10^{-11} to $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1.0 to $0.025 \text{ ppb}^{-1} \text{ s}^{-1}$) [see Table 2 and ref 2)]. At $6.7 \times 10^{-6} \text{ ppb OH}$, the pseudo-first-order rate constants ($k \times [\text{OH}]$) for these reactions are in the range of 7×10^{-6} to $2 \times 10^{-7} \text{ s}^{-1}$. Hence, for the conditions stated, the OH-mediated pathways for the oxidation of saturated organics proceed 2–5 orders of magnitude faster than the O_3 pathway (although OH oxidation of saturated organics is still relatively slow compared to air exchange). In other words, by transforming a fraction of indoor O_3 to indoor OH, the O_3 /alkene reactions transform a kinetically-limited oxidizing environment to a kinetically more favorable one.

At concentrations in the range of 10^{-6} to 10^{-5} ppb , OH will have only a small influence on the indoor concentrations of the compounds listed in Table 2. However, reactions between OH and common indoor species can significantly influence the indoor concentrations of the resulting products. These include aldehydes, ketones, organic acids, and inorganic acids (the latter generated from the OH/ NO_2 and OH/ SO_2 reactions). In the absence of OH-initiated chemistry, some of the products might not be present indoors.

The ramifications of larger or smaller indoor OH concentrations are, at present, not well understood. Oxidation of outdoor VOCs increases their water solubility and the rate at which they are removed from the atmosphere by precipitation. Oxidation of indoor VOCs does not appear to produce a comparably beneficial outcome. Indeed, the resulting indoor oxidation products may be more irritating to human occupants and more corrosive to materials, including expensive electronic equipment and cultural artifacts, than the compounds from which they are derived. In buildings with sensitive human occupants or where corrosion is a major concern, it may be prudent to avoid the simultaneous presence of O_3 and alkenes at elevated concentrations.

A recent study by Sundell et al. (44) measured total VOC (TVOC) concentrations in the supply air as well as TVOC and formaldehyde concentrations in the room air of 29 office buildings. The occurrence of occupant complaints was high in 14 of these buildings and low in the remaining 15. In a number of the buildings, the mean TVOC concentrations in the room air were significantly lower than in the supply air. The "loss" of TVOC from supply to room air correlated with larger concentrations of formaldehyde and an increased number of occupant complaints. The authors speculate that this observation may reflect partial transformation of less irritating nonpolar VOCs to more irritating polar VOCs. (The analytical procedures used to measure TVOC are less sensitive to polar VOCs than to nonpolar VOCs.) If so, indoor OH may play a role in the transformation process.

While our analysis predicts occasions when the indoor concentration of the hydroxyl radical approaches or surpasses 10^{-5} ppb ($2.5 \times 10^5 \text{ molecules/cm}^3$), this remains conjecture. Experiments are necessary to establish the presence of indoor OH. Even if OH is not detected indoors,

the result would be significant since it would indicate that our current understanding of indoor chemistry is incomplete.

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