Recent Advances in Indoor Chemistry

Glenn Morrison [1]

Abstract Just as the chemistry creates urban smog and aerosols that influence climate change, chemistry in building air can alter the indoor environment for better or worse. This review focuses on chemical pathways initiated by oxidants that infiltrate from outdoor air and other indoor-sourced reactants and surfaces that make these environments unique chemical reactors. Ozone reacts with fragrance molecules, tobacco smoke residues, and even human skin oils to generate a host of oxidized organic compounds, secondary organic aerosols, and irritants. Nitrous acid is formed on indoor surfaces and is subsequently cleaved by even the relatively dim light indoor. This raises the indoor concentration of the highly reactive hydroxyl radical. Nitrous acid can also react with tobacco smoke residue to form carcinogenic nitrosamines. Some seek to harness this chemistry to help reduce indoor concentrations of unwanted indoor pollutants using novel surface coatings, but controlling that chemistry is challenging.

Introduction

Any discussion of sustainable building environments must include the health, welfare, and productivity of the occupants,

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for without that buildings are fundamentally flawed. Indoor air quality and the chemistry that takes place in buildings affect occupants in ways that are still poorly understood. This paper reviews the more recent advances in our understanding of what chemistry occurs and touches on how this chemistry could affect occupants. This review distinguishes between "chemicals" and "chemistry." Chemicals that are simply released or drawn into indoor environments but do not take part in chemical transformations are not included.

Indoor chemistry has been the subject of scientific investigations for several decades, but these have been relatively sparse compared with the thousands of studies on outdoor air chemistry. In his review of 20 years of research, Weschler [1] identified only about 270 indoor chemistry publications between 1991 and 2010. However, as Weschler points out, the much more intensive study of ambient air chemistry has informed our understanding of indoor chemistry. Therefore, a much richer set of resources is available to guide targeted research in indoor environments.

All chemical reactions occurring in the outdoor atmosphere are possible indoors. However, key differences in conditions alter the extent to which these reactions can occur in buildings. Much outdoor chemistry is driven directly by photolytic energy of the sun. Although sunlight through windows can initiate chemistry, indoor environments are dimmer. Compared with the outdoor atmosphere, there is much more surface area available indoors to support interfacial chemistry. Air exchanges within hours in a building, rather than the day or weeks that some species can spend in the atmosphere. Finally, the indoor and outdoor concentrations of many organic and inorganic species differ by one or more orders of magnitude. Taken together, the composition of indoor air can be very different. Combined with the fact that people spend so much more time in buildings than outside, the impact of indoor chemistry on health and welfare is of concern.

This brief review will focus on results of the past 5–10 years. There have been several reviews of indoor chemistry in recent years, including the exceptional overview by Weschler in 2011 [1]. I hope that this paper serves to enrich this prior literature without unnecessarily repeating what has already been reported in previous reviews. However, to put recent research in context, it will be necessary to highlight key research from the past.

Ozone and Related Chemistry in Air

In the context of urban smog, ozone (O_3) chemistry has been studied extensively since the 1950s. Ozone is formed in a photocatalytic reaction involving sunlight, nitrogen oxides, and organic compounds. During the daytime, ozone is typically present at air concentrations in the tens of parts per billion but can exceed 100 ppb in particularly polluted urban areas. Ozone is highly reactive and will oxidize unsaturated organic compounds to form a large number of products including stable carbonyls such as formaldehyde, short-lived oxidized organic species, highly reactive free radicals, and even aersols (i.e., secondary organic aerosols). Ozone also reacts with nitrogen oxides, unsaturated organic compounds, and other species. Some radical products of these reactions can further react with organics and inorganics to produce further generations of oxidation products. The full picture is highly complex and worthy of over half a century of intensive research. The next step was to apply this knowledge to indoor environments.

In 1993, Nazaroff and Cass [2] developed a mass balance model of indoor air that included chemistry and concluded that much of the chemistry happening outdoor could occur indoors at relevant rates. Weschler and Shields [3] then showed that ozone will react with terpenes at substantial rates in indoor environments. Since that time, ozone and its reactions with terpenes have been among the most well-studied chemistry in the context of indoor air. Some terpenes exist at much higher concentrations indoors because they are emitted by wood, cleaners, air fresheners, and personal care products [4–6]. Interest in better understanding this chemistry in indoor environments led to kinetic studies of ozone-terpene reactions specifically relevant to indoor environments (e.g., α-terpineol [7]), observation of secondary organic aerosol formation in lab and field studies [3, 8], and identification of formaldehyde and other undesirable gas-phase products [9]. Rosignol et al. have recently reported field measurements of 35 distinct chemical products of these reactions using modern concentration and derivatization methods [10].

Our current understanding of how this research translates to indoor environments has accelerated in recent years. A central idea is emerging that the outcomes of indoor chemistry are highly dependent on conditions. Building environments are highly heterogeneous: one home is not like the next, and the range of variability in compound concentrations, temperature, relative humidity, and air exchange is wide. Combined with the large number of reactants, products, secondary reactants, and side reactions (Fig. 1), each microenvironment has a unique chemical signature. On the shoulders of early models and experimental research, contemporary chemical models, lab studies, and field research are revealing novel insights.

Fig. 1 Major reactants, products, and pathways of indoor chemistry
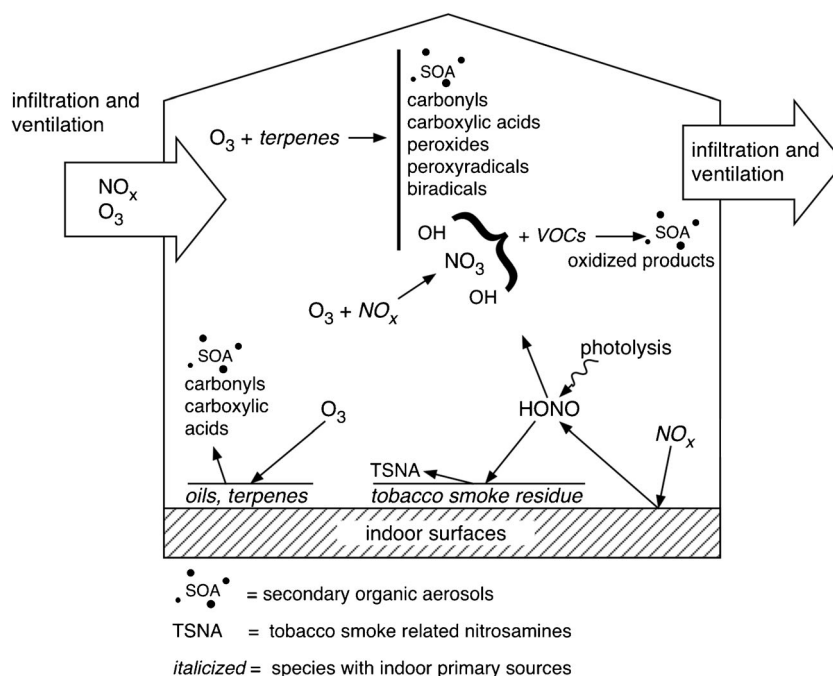
The objective of models of indoor chemistry is to predicting yields of health-related products such as peroxides, irritants, and aerosols. One of the key findings has been that such chemistry is very sensitive to conditions that vary widely among indoor environments. The initial concentrations of ozone, nitrogen oxides, terpenes, other organics, light intensity, and spectral detail strongly influence the outcomes. Carslaw et al. updated a previous model to include identification of over 140 explicit species, radicals, and secondary aerosol formation [11, 12•]. In 2013, Carslaw applied that model to follow limonene oxidation pathways in detail during simulated cleaning activities [13]. The model predicts that carbonyls and peroxyacetyl nitrates are the most common gas-phase species formed. In aerosols, peroxides, carbonyls, and organic nitrates dominate. At higher ozone concentrations, organic acids and alcohols begin to become important in the gas phase, reflecting a shift towards more ozone-dominated oxidation, relative to OH radical oxidation. Youssefi and Waring modeled secondary organic aerosol (SOA) formation and found that yield is likely to be highly variable indoors and sensitive to ozone and background organic aerosol concentrations [14].

Measurements bear out the general theme that initial conditions significantly influence outcomes. Water (humidity) and nitrogen oxides have been found to influence the production of SOA [15, 16]. Initial ozone and terpenoid concentrations influence the number and mass concentrations of SOA formed [17]. Pathak et al. found that including an organic compound that scavenged OH created conditions such that the volatility of SOA was influenced by ozone concentrations [18]. In indoor environments, there are many VOCs other than terpenes that can act to scavenge OH. Ammonia, emitted from sources as diverse as cat litter boxes and cleaners, can also influence SOA generation. Organic acids generated by ozone-terpene chemistry can combine with ammonia to grow or nucleate SOA [19]. However, this sensitivity to initial conditions is not true of all chemical outcomes. In ozone reactions with terpene mixtures, Forester and Wells [20] did not observe any influence of humidity on the yield of hydroxyl radicals.

Surface Chemistry

Surfaces in buildings can increase apparent rates of reactions, provide unique environments for reactions to take place, and increase the interaction time between chemical reactants [21]. The surfaces are not simply the polyvinylchloride of some flooring, wood, nylon, or brick. All of these unique materials are also coated in adsorbed molecules and/or rather thickly coated in films comprised of high-molecular-weight organics (e.g., oils), salts, water, and numerous other contaminants. Contemporary studies have focused on reactions with (or influenced by) the base materials, coatings, and adsorbed molecules.

Base materials as diverse as brick, wood, carpet, and clothing have all been evaluated for their ability to remove ozone and potential to generate volatile by-products. In general, inorganic substrates tend to remove ozone without byproducts and the ozone removal rate tends to increase with available surface area. Organic or polymer-based substrates have tended to generate more volatile carbonyl byproducts, but this may be due to more oily coatings than to low-reactivity polymers that make up the substrate.

For example, Coleman et al. found that clothing is a source of ozone-generated secondary carbonyl emissions, likely due to reactions with fatty acids and skin oils [22]. More recently, Rai et al. observed similar carbonyl products in ozone-initiated surface chemistry with cotton t-shirts previously worn by subjects [23]. They also observed higher secondary emissions at higher relative humidity.

Many studies have shown that molecules adsorbed to aerosol surfaces can react with ozone at rates that exceed those for the gas-phase reactions (e.g., benzo[a]pyrene and ozone [24]). The rate at which molecules can react indoors overall can also be enhanced at surfaces. On glass and PVC surfaces, Δ^3-carene and limonene react with ozone 10–100 times faster than in the gas phase [25]. For lower volatility terpenoids such as α-terpineol and dihydromyrcenol, higher adsorbed mass combined with higher relative reaction rates mean that more of these species become oxidized by surface chemistry than by gas-phase chemistry [26, 27]. Further, the yield of reaction products can differ from the gas-phase reaction [28]. Looking beyond individual molecules to mixtures, Destaillats et al. showed that residual compounds left on surfaces after cleaning would increase ozone surface reactivity and generate gas-phase reaction products [9]. Ozone will also react with tobacco smoke residuals on indoor surfaces and generate volatile products such as cotinine [29]. A related, important, finding is that HONO will react with tobacco smoke residue on surfaces and produce carcinogenic tobacco-specific nitrosamines [30•].

In addition to volatile by-products, aerosols can also form upon reaction of ozone with reactive species on surfaces [9]. Several recent studies have observed particle generation that results from ozone reacting with specific surface-associated molecules, such as squalene [31], limonene [32], and nicotine [30•, 33], or with clothing [34] and HVAC filters [35]. In general, the particles generated are in the ultrafine size range (<100 nm). The particles generated are unique to these sources, can increase number concentrations, and therefore could have unique health consequences. In recent field studies, Reche et al. measured ultrafine particles indoors and outdoors [36]. They suggested that some sources could be surface-mediated production of ultrafine particles because

indoor/outdoor number concentration ratio of smaller particles was higher at higher outdoor ozone concentrations.

The HONO that was responsible for generating tobacco-specific nitrosamines [30•] can itself be formed at indoor surfaces. HONO is an important compound that "stores" the highly reactive OH radical. The radical is generated by photolysis of HONO, and this can occur even in the dim light of indoor environments. In 1985, Pitts et al. showed that NO_2 can deposit on indoor surfaces and convert to volatile HONO that can generate indoor levels that exceed outdoor levels when NOx is released from gas burners [37]. Several recent studies are demonstrating that HONO formation rates may be enhanced by light. Gomez-Alvarez et al. observed high HONO levels indoors and attributed them to light-induced formation at indoor surfaces [38•]. Later lab studies on painted surfaces and surfaces with cleaner residue observed formation rates that were consistent with field observations [39, 40].

Building Characteristics

Building structure, surfaces, operation, environmental conditions, and so forth can all influence indoor chemistry and the extent to which specific reactions proceed. This increasing understanding of the relationships between building physics and chemistry will be important in controlling chemistry and better understanding population exposure to the results of indoor chemistry.

Several papers have reported on the relationship between building ventilation, recirculation, and filtration on the resulting concentration of ozone, terpenes, and secondary organic aerosols [41–43]. Several general findings have emerged: Increasing exchange of ozone-containing outdoor air (ventilation) increases ozone and increases SOA up to a point, but then SOA decreases with further increases in ventilation; recirculation through particle and/or ozone filters reduces SOA. Use of stand-alone ionizing air cleaners increases indoor ozone and thereby increases terpene oxidation and resulting SOA formation [44].

There has been increasing interest in the use of indoor surfaces, and surface chemistry, as the means to control indoor air pollutants. Typical indoor environments have a large surface area-to-volume ratio and a relatively slow air exchange rate. This means that an indoor gas molecule may strike an indoor surface many thousands, or even millions, of times before being removed by ventilation. Because ozone initiates so many undesirable reactions, it is desirable to identify materials that passively remove ozone without also generating by-products [45]. Activated carbon and clay-based wall coatings appear to be effective at removing ozone [46–48] and can continue to be effective when placed for extended periods in buildings [49]. In a human subject study, Darling et al. found that use of clay-coated panels in a room improved perceived air quality in a chamber with carpet and injected ozone [50]. Only recently have more fundamental studies of relevant materials begun to link ozone removal with physical characteristics such as porosity and surface area [51].

Control of VOCs via surface chemistry has also been of rising interest, especially using photocatalytic materials such as TiO_2. Salthammer and Fuhrmann found that commercially available photocatalytic paints were able to reduce concentrations of formaldehyde and NO_2 using sunlight simulating lamps [52]. In field experiments, Auvinen and Wirtanen found that photocatalytic paints can actively convert compounds, but undesirable by-products are formed [53]. Recently, Gandolfo et al. showed that removal of NO_2 can be accompanied by formation of HONO, which can initiate undesirable oxidation chemistry upon photolysis of HONO [54]. Advances continue to be made in the performance of photocatalysts under indoor lighting conditions but by-product formation remains a challenge.

The Impact of the Presence of People

An intriguing area of research has emerged around the idea that occupants influence the ozone chemistry in buildings. Several studies have shown that ozone chemistry taking place on clothing [22, 23, 55], skin [56•], and hair [57] reduce indoor concentrations of ozone and increase gas-phase and aerosol reaction products associated with occupant surface chemistry. Ozone reacts with fatty acids and squalene in human skin oils (sebum) and generates a suite of products such as acetone, nonanal, 4-oxopentanal, and 6-methyl-5-hepten-2-one. In the microenvironment surrounding a person, this chemistry lowers ozone levels and increases product concentrations, thereby influencing inhalation exposure [58]. In recent work with human subjects, Fadeyi et al. showed that occupants in a chamber reduce SOA concentrations that result from limonene-ozone reactions, primarily because they are reducing indoor ozone concentrations by reaction at the skin and clothing surfaces [59].

Health

Perhaps one of the least well-understood, but vital, issues is the impact of indoor chemistry on human health. The formation of by-products from the reaction of ozone with terpenes has prompted a number of in vitro, animal, and human studies. For an excellent recent discussion of health studies related to ozone-terpene chemistry, please see Rohr's review [60]. Early mouse studies of reactions of ozone α-pinene [61] and d-limonene [62] suggested that products acted as airway irritants. Some multifunctional compounds such as dicarbonyls

[63] and gas-phase biradicals [64] have been suggested as being responsible.

Peroxides formed are also of concern as they constitute "reactive oxygen species" or ROS that may result in more chronic health problems. ROS is linked to oxidative stress which may lead to pulmonary diseases and cancer. Anderson et al. [65] found that cell proliferation decreased in epithelial cells (in vitro) when exposed to limonene-ozone mixtures that were at a high concentration relative to typical indoor environments. They inferred that products of the ozonation chemistry were responsible. Fadeyi et al. exposed asthmatics and non-asthmatics to either clean air or air with limonene-ozone (and their respective reaction products) and studied perception, work performance, and physiological characteristics [59]. They found that the level of α-amylase (a stress indicator) in saliva increased with exposure to the limonene-ozone mixture. Chen and Hopke [66–68] studied the SOA and ROS generated by the reactions of ozone with α-pinene and limonene. They found quantifiable levels of ROS, measured as the hydrogen peroxide equivalent, suggesting that this chemistry could have adverse health endpoints. Kurshid et al. measured ROS, such as peroxides, in aerosols in 12 residential and 11 commercial and retail buildings [69]. They found that the indoor concentration of ROS was similar to that outdoors and that there were no clear associations with other measured species (PM, VOCs, ozone). They recommended that ROS be measured independently, as its concentration cannot yet be inferred from other species.

Conclusions

This research field is still very young and there are many opportunities for discovery. The following are just a few areas that have been noted by others or are of particular interest.

– Most indoor air chemistry models include surface chemistry in the form of deposition and subsequent removal of compounds or aerosols. Although some information exists on the yield of some products from ozonation at surfaces such as carpet, paint, or clothing, models do not include explicit mechanistic predictions of the chemistry or kinetics necessary to predict formation of new products at the surface. Indoor surfaces are highly heterogeneous and a deep understanding of their composition and local environmental conditions will be necessary to make such predictions. A better understanding of local adsorption phenomena will also be helped by improved surface composition information: note that sorption of basic amines such as nicotine is sensitive to humidity, CO_2, and ammonia [70]. It is likely that this is also true for organic acids and other species that undergo acid-base chemistry.

– There has been growing interest in using advanced analytical techniques, originally designed for outdoor atmospheric chemistry research, to study indoor environments. Examples include proton-transfer chemical-ionization mass spectrometry (PTRMS) [55] to obtain real-time concentrations of VOC reaction products, light-induced fluorescence-fluorescence assay by gas expansion (LIF-FAGE) [38•] for direct measurement of OH and HO_2 radicals, and cavity ring-down spectroscopy for measurement of the nitrate radical [71]. There are many more opportunities to advance this field using well-established instrumentation and more recent innovative instruments.

– Recent observations of high OH concentrations indoors, possibly related to photolysis of HONO, have suggested more detailed studies of the spectral intensity due to sunlight penetration through windows, changes in window glazing, and a changing landscape of indoor lighting (CFL, incandescent, LED) [72].

– MacLean et al. found that lead in house dust weathers to become more bioavailable over several months of exposure to typical temperature and humidity [73]. How does such aging under the unique conditions in buildings influence the bioavailability of other metals tracked in on shoes or deposited from outdoor air ventilation?

– Buildings that have excessive mold growth and been contaminated with pathogenic organisms or toxic chemicals can be decontaminated in many ways, with uncertain chemical outcomes. For example, Corsi and Poppendieck investigated the use of very high levels of ozone and chlorine dioxide as a disinfectant and observed persistent emissions of carbonyl compounds, and even chlorinated by-products, long after the ozonation event [74, 75]. Ozone and ClO_2 continue to be promoted for disinfection without sufficient follow-up on the impact on indoor air quality of such methods.

– Microorganisms in buildings also are responsible for changing indoor environments, including the chemicals present. There has been a surge of interest in understanding the indoor microbiome [76]. These organisms grow, respire, and can release the by-products of their biochemistry into the indoor environment. For example, Inamdar et al. showed that a 1-octen-3-ol, a "mushroom alcohol" generated by indoor fungi, reduced uptake of dopamine in human cell lines and suggests that it could represent an environmental agent involved in Parkinson's disease [77].

This review has touched on much of the existing information on indoor chemistry as it relates to air quality, but is necessarily of limited scope. Future reviews of indoor chemistry will likely need to focus on specific topics within this field to synthesize the material in a substantive fashion. I look

forward to those reviews and the new discoveries in this rap-idly growing research field.

Compliance with Ethics Guidelines

Conflict of Interest Glenn Morrison declares that he has no conflict of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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