Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry

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Abstract

The variety of chemical substances present in modern building products, household products and furnishings provides potential for chemical reactions in the material (case 1), on the material surface (case 2) and in the gas phase (case 3). Such “indoor chemistry” is known as one of the main reasons for primary and secondary emissions. The conditions of production often cause unwanted side reactions and a number of new compounds can be found in finished products. Elevated temperatures are responsible for the degradation of cellulose, decomposition of non-heat-resistant additives and other thermally induced reactions like Diels–Alder synthesis. Heterogeneous chemistry takes place on the surface of materials. Well-known examples are the formation of aliphatic aldehydes from the oxidation of unsaturated fatty acids or the cleavage of photoinitiators under the influence of light. In case of composite flooring structures hydrolysis is one of the major pathways for the appearance of alcohols from esters. If different kinds of material are fixed together, emissions of new VOCs formed by inter-species reactions are possible. Other indoor air pollutants are formed by rearrangement of cleavage products or by metabolism. Compounds with –C=–C– bonds like terpenes, styrene, 4-phenylcyclohexene, etc. undergo gas phase reactions with O3, NOx, OH and other reactive gases. It has been shown that such products derived from indoor-related reactions may have a negative impact on indoor air quality due to their low odor threshold or health-related properties. Therefore, the understanding of primary and secondary emissions and the chemical processes behind is essential for the evaluation of indoor air quality. This publication gives an overview on the current state of research and new findings regarding primary and secondary emissions from building products and furnishings.

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Keyword index: Building products; Chemical reactions; Primary and secondary emissions; Indoor chemistry

1. Introduction

“Are we measuring the relevant indoor pollutants”? This provocative and rhetorical question is the title of a publication by Wolkoff et al. (1997), which examines the negative influence on human health caused by reactive substances and secondary products in indoor air. The authors deal with a topical branch of indoor research known as “Indoor Chemistry”, but which has now achieved general attention. Wolkoff et al. (1997) contended in their publication cited above, that especially reactive organic compounds and their reaction products can have an
influence on human well-being even in low concentrations and therefore make a significant contribution to the sick-building-syndrome (SBS). Furthermore, indoor air contains many highly reactive molecules and radicals such as ozone (O₃), nitrogen oxides (NOₓ), hydroxyl radicals (OH) and sulfur dioxide (SO₂), that are either introduced from the outside air or generated directly indoors by human activities (photocopiers, laser printers, gas cookers, UV lighting, etc.). Mechanisms and kinetics of gas-phase reactions in the outdoor atmosphere have been studied for decades (Atkinson and Carter, 1984; Finlayson-Pitts and Pitts, 2000), but comparatively late researches have investigated such reactions under the special conditions of the indoor environment (see Section 3) and their impact on human health and perceived air quality. Allen et al. (1978) have recognized the relevance of indoor ozone concentrations and have characterized potential sources. A general mathematical model to compute the concentrations of chemically reactive substances in indoor rooms was presented by Nazaroff and Cass (1986). Modeling of VOC emissions from building products mainly focused on primary compounds (Little et al., 1994). Lee et al. (2005) have presented an analytical model to predict both primary and secondary VOC source or sink behavior of porous building materials. The model considers diffusion and adsorption/desorption within the material and provides the effects of material properties and airflow properties on the primary and the secondary behavior. Systematic experimental investigations on the topic of indoor chemistry became known at the beginning of the 1990s by the work of Weschler et al. (1992) on aldehyde emission from carpet in the presence of ozone. In a more recent paper, Weschler and Shields (1997) determined the following: “From a chemical perspective, the indoor environment is a reaction vessel with chemicals continually entering and exiting. Some of these chemicals can react with one another (or themselves) creating reaction products that might otherwise be absent from the indoor setting. Many of the resulting products are more reactive and/or irritating than their precursors”. At the Healthy Buildings 2000 conference, “primary” and “secondary” emissions (resulting from chemical transformations) were the main focus of a workshop on the assessment of material emissions (Salthammer and Kephalopoulos, 2000). Papers from the Indoor Air Conference 2002 on “Indoor Chemistry and Physics” were selected for a special issue of Atmospheric Environment (Nazaroff et al., 2003). The indoor chemistry discussion intensified during the “Indoor Chemistry and Health Workshop”, which was held in Santa Cruz, CA in 2004 (Weschler et al., 2005) and later at the Indoor Air 2005 Conference with a Forum on “Recent Advances in Indoor Chemistry” (Weschler and Salthammer, 2005). Today, indoor chemistry is a well-established topic of indoor research (Weschler, 2004; Weschler and Wells, 2004; Sundell, 2004).

From the papers published in recent years on the subject of indoor chemistry the following major aspects can be derived:

(a) gas-phase reactions;
(b) emissions of primary and secondary products from single materials and combined materials;
(c) impact of reactive species and reaction products on human health.

Many building materials, furnishings and household products demonstrate emission of volatile organic compounds (VOCs) during usage (Salthammer, 2004) and have been documented as sources of reactive compounds and reaction products. The problem might become dominant when components of different materials can react with each other. This effect can be exemplified for the case of a typical flooring structure: Both, adhesive and floor covering could be ranked as low emitting materials under the conditions of a “single-product” chamber test as proposed by AgBB—Committee for Health-related Evaluation of Building Products (2005). However, the pattern of emitting species and emission rates looks different under “real-world” conditions due to interactions between flooring material, adhesive and concrete (Salthammer et al., 2004; Wilke et al., 2004). A number of different factors can influence the emission characteristics (Wolkoff, 1998, 1999) and numerous investigations have shown that indoor chemistry is of particular importance for the indoor-related evaluation of building products. The reactants and products as well as possible sources discussed in this paper are summarized in Table 1. Test chamber studies on primary and secondary emissions from building products can be found in Table 2.

2. Classification of primary and secondary emission sources

During the Healthy Buildings Conference 2000, possible definitions of primary and secondary emissions were presented (Salthammer and Kephalopoulos, 2000):
Primary emission: The physical release of compounds which are present in a new product.

Secondary emission: Compounds produced by chemical reaction in the product or in the indoor environment.

Wolkoff et al. (2005) have proposed to subdivide VOCs into four categories: (i) chemically non-reactive, (ii) chemically reactive, (iii) biologically reactive and (iv) toxic.

In Fig. 1, the generation of primary and secondary emissions from building products is described and three different cases can be discussed:

Case 1: An unwanted reaction is happening during the production of a material and the formed reaction product is released at the customers site.

Case 2: An unwanted reaction is happening at the surface or in different materials at the customers site, e.g. between concrete, adhesive and flooring material.

Case 3: An unwanted reaction of primary compounds with other primary compounds or reactive gases is happening in the gas phase at the customers site.

Emission sources generated according to case 1 are often related to the conditions of the production process or to an inadequate composition of the product. Generally, only the producer can influence such emissions and after a full analysis of the raw materials and emission products it is often possible to avoid undesired side reactions during production.

Table 1
Possible reaction products in indoor air with potential emission sources and reactants

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Possible source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-pinene</td>
<td>Pinene oxide, pinonaldehyde</td>
<td>Wood, wood-based products</td>
</tr>
<tr>
<td>Limonene</td>
<td>Limonene oxide, carvone, formaldehyde</td>
<td>Wood, coating systems</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>Heptanal, octanal, nonanal, decanal, 2-decanal</td>
<td>Linoleum, eco-lacquers, nitrocellulose-lacquers, alkyd resins</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>2-pentenal, 2-hexenal, 3-hexenal, 2-heptenal, 2,4-heptadienal, 1-penten-3-one</td>
<td></td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>Hexanal, heptanal, 2-heptenal, octanal, 2-octenal, 2-nonenal, 2-decenal, 2,4-nonadienal, 2,4-decadienal</td>
<td></td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>Furfural, acetic acid</td>
<td>Cork</td>
</tr>
<tr>
<td>PHMP</td>
<td>Benzaldehyde, acetone, benzil</td>
<td>UV-cured coatings</td>
</tr>
<tr>
<td>HCPK</td>
<td>Benzaldehyde, cyclohexanone, benzil</td>
<td>UV-cured coatings</td>
</tr>
<tr>
<td>2-ethyl-hexyl acetate</td>
<td>Acetic acid, 2-ethyl-1-hexanol</td>
<td>Solvent</td>
</tr>
<tr>
<td>Zn-2-ethylhexanoate</td>
<td>2-ethyl-1-hexanoic acid</td>
<td>Stabilizers</td>
</tr>
<tr>
<td>n-butylacrylate</td>
<td>n-butanol</td>
<td>Acrylate coatings</td>
</tr>
<tr>
<td>DEHP</td>
<td>2-ethyl-1-hexanol</td>
<td>Plasticiser</td>
</tr>
<tr>
<td>DBP</td>
<td>2-butanol</td>
<td>Plasticiser</td>
</tr>
<tr>
<td>DIBP</td>
<td>2-butanol</td>
<td>Plasticiser</td>
</tr>
<tr>
<td>TCP</td>
<td>1-chloro-2-propanol, 2-chloro-1-propanol</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>TDCPP</td>
<td>1,2-dichloropropene, 1,2-dichloropropanol</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>TCEP</td>
<td>2-chloro-ethanol</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>TBPP</td>
<td>1-bromo-2-propanol, 2-bromo-1-propanol</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>TDBP</td>
<td>2,3-dibromo-1-propanol</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>Styrene + cis-1,3-butadiene</td>
<td>4-phenyl-cyclohexene (4-PCH)</td>
<td>SBR</td>
</tr>
<tr>
<td>Cis-1,3-butadiene + trans-1,3-butadiene</td>
<td>4-vinyl-cyclohexene (4-VCH)</td>
<td>SBR</td>
</tr>
<tr>
<td>2-chloro-1,3-butadiene</td>
<td>1-chloro-4-(1-chlorovinyl)-cyclohexene</td>
<td>Rubber</td>
</tr>
<tr>
<td>Zn-diethyldithiocarbamate</td>
<td>CS₂, diethyamine</td>
<td>Vulcanization accelerator</td>
</tr>
<tr>
<td>Azodicarbonamide</td>
<td>Semicarbazide</td>
<td>Foaming agent</td>
</tr>
<tr>
<td>Adipinic acid + 1,4-butanediol</td>
<td>1,6-dioxacyclododecan-7,12-dione</td>
<td>Adhesive</td>
</tr>
<tr>
<td>Dimethylaminoethanol + formic acid</td>
<td>Dimethylformamide</td>
<td>“Green” paint</td>
</tr>
<tr>
<td>L-tryptophane</td>
<td>o-aminocyclohexanone</td>
<td>Casein products</td>
</tr>
<tr>
<td>2,3,4,6-tetrachlorophenol</td>
<td>2,3,4,6-tetrachloroanisole</td>
<td>Application of PCP</td>
</tr>
<tr>
<td>T4MDD</td>
<td>MIBK, 3,5-dimethyl-1-hexyne-3-ol</td>
<td>Water-based paint</td>
</tr>
<tr>
<td>AIBN</td>
<td>Tetramethyl succinonitrile</td>
<td>Flexible PU foam</td>
</tr>
</tbody>
</table>

See text for abbreviations.
The situation described in case 2 is usually more difficult to resolve. Materials can be combined during production steps or at the customers site. When encountering such a case it is difficult to find out if the substance causing complaints is a primary or a secondary emission of a certain product. If a primary emission can be excluded, the difficult search for possible precursors and reaction pathways starts. If reactive components like O$_3$, NO$_x$ an OH are present in indoor air, secondary emissions formed according to case 3 can often be identified. However, for some common types of reaction like hydrolysis it might be difficult to separate gas-phase reactions from prior moisture damage of the material.

The following table provides an overview of test chamber studies on primary and secondary emissions from building materials:

<table>
<thead>
<tr>
<th>Building product</th>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpet</td>
<td>Ozone</td>
<td>Weschler et al. (1992)</td>
</tr>
<tr>
<td>Carpet</td>
<td>Ozone</td>
<td>Sollinger et al. (1993; 1994)</td>
</tr>
<tr>
<td>Linoleum</td>
<td>Ozone</td>
<td>Jensen et al. (1995a; b)</td>
</tr>
<tr>
<td>Latex paint</td>
<td>Ozone</td>
<td>Reiss et al. (1995b)</td>
</tr>
<tr>
<td>Wallcovering, latex paint, carpet, plaster, plywood</td>
<td>Air velocity, humidity, temperature, air</td>
<td>Wolkoff (1998)</td>
</tr>
<tr>
<td>PVC, parquet, carpet, sealant, paint</td>
<td>Air velocity</td>
<td>Horn et al. (1998)</td>
</tr>
<tr>
<td>Cork products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC, parquet, carpet, sealant, paint</td>
<td>Temperature, humidity</td>
<td>Knudsen et al. (1999)</td>
</tr>
<tr>
<td>Wood-based furniture coatings</td>
<td>Complete floor structures</td>
<td>Salthammer et al. (1999)</td>
</tr>
<tr>
<td>Carpet, PVC flooring, sealant, floor varnish, wall paint</td>
<td>Light</td>
<td>Fang et al. (1999)</td>
</tr>
<tr>
<td>PVC, adhesive</td>
<td>Ozone</td>
<td>Sjöberg (2000)</td>
</tr>
<tr>
<td>Particle board, MDF</td>
<td>Ozone</td>
<td>Baumann et al. (1999, 2000)</td>
</tr>
<tr>
<td>UV-cured lacquer</td>
<td>Heat-treatment</td>
<td>Salthammer et al. (2002)</td>
</tr>
<tr>
<td>Wood</td>
<td>Ozone</td>
<td>Manninen et al. (2002)</td>
</tr>
<tr>
<td>Carpet</td>
<td>Ozone</td>
<td>Morrison and Nazaroff (2002)</td>
</tr>
<tr>
<td>Wood-based products, laminate, cork, adhesive, lacquer</td>
<td>Complete floor structures</td>
<td>Knudsen et al. (2003)</td>
</tr>
<tr>
<td>Adhesives, PVC, linoleum, rubber, polyolefine</td>
<td>Complete floor structures</td>
<td>Salthammer et al. (2004)</td>
</tr>
<tr>
<td>UV-coating</td>
<td>Light</td>
<td>Wöike et al. (2004)</td>
</tr>
<tr>
<td>PVC, adhesive</td>
<td>Ozone</td>
<td>Knudsen et al. (2003)</td>
</tr>
<tr>
<td>Particle board, MDF</td>
<td>Complete floor structures</td>
<td>Salthammer et al. (2004)</td>
</tr>
<tr>
<td>Wood-based products, laminate, cork, adhesive, lacquer</td>
<td>Complete floor structures</td>
<td>Wilke et al. (2004)</td>
</tr>
<tr>
<td>Adhesives, PVC, linoleum, rubber, polyolefine</td>
<td>Light</td>
<td>Salthammer et al. (2002)</td>
</tr>
<tr>
<td>UV-coating</td>
<td>Ozone</td>
<td>Salthammer et al. (2002)</td>
</tr>
</tbody>
</table>

Fig. 1. Formation of primary and secondary emissions from chemical constituents of materials for indoor use.
3. Mechanisms of secondary emission generation

3.1. Reactive gases as causes for secondary emissions

The major pathways for removal of airborne VOCs emitted from an indoor source are air exchange and deposition in an irreversible sink. Both kinetic processes are of first order and can be in the same order of magnitude or even faster in comparison to chemical reactions (which usually follow a bimolecular kinetic law) under indoor conditions. The parameters, which mainly influence the effectiveness of gas-phase reactions in indoor air have been described by Weschler and Shields (1997). Reaction schemes, which should be of relevance for the indoor environment are listed below. It was postulated that Eqs. (1) and (2) might be the main reaction pathways in indoor air for decomposition of ozone, generating NO₂ and NO₃ in significant amounts.

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \]  
(1)

\[ \text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2 \]  
(2)

\[ \text{NO}_3 + \text{R} - \text{H} \rightarrow \text{HNO}_3 + \text{R} \]  
(3)

\[ \text{OH} + \text{R} - \text{H} \rightarrow \text{H}_2\text{O} + \text{R} \]  
(4)

\[ \text{O}_3 + \text{R}_1\text{R}_2\text{C} = \text{CR}_3\text{R}_4 \rightarrow [\text{ozonide}]^* \]  
(5a)

\[ [\text{ozonide}]^* \rightarrow \text{R}_1\text{C}(\text{O})\text{R}_2 + [\text{R}_3\text{R}_4\text{COO}]^* \]  
(5b)

\[ [\text{ozonide}]^* \rightarrow \text{R}_3\text{C}(\text{O})\text{R}_4 + [\text{R}_1\text{R}_2\text{COO}]^* \]  
(5c)

The gas-phase reaction of ozone with unsaturated hydrocarbons is known to produce aldehydes, ketones and acids as main components (Atkinson, 1995; Atkinson et al., 1995a; Grosjean and Grosjean, 1998; Reiss et al., 1995a). In the initial step (5a), a primary ozonide is formed, which is not stable. Reactions (5b) and (5c) then lead to a Criegee biradical, which may decompose or rearrange under formation of OH via the hydroperoxide channel. In Eqs. (5a)–(5c) the asterisk indicates excess internal energy. More detailed information on gas-phase reactions and bimolecular rate constants can be obtained from Atkinson and Carter (1984), Atkinson (2000), Finlayson-Pitts and Pitts (2000), Colbeck and McKenzie (1994). Common indoor sources of unsaturated hydrocarbons were compiled by Weschler and Shields (1997). Several authors have measured and/or calculated indoor concentrations of reactive gases (Brauer et al., 1993; Drakou et al., 1998; Sørensen and Weschler, 2002; Vingarzan, 2004; Weschler, 2000; Weschler and Shields, 2000; Zhang and Lioy, 1994). Typical concentration ranges in indoor air are summarized in Table 3. It is an interesting side note that the nowadays increasingly used air cleaning devices can be substantial sources of ozone in rooms (Hubbard et al., 2005). It was estimated that the peroxyacetyl nitrate (PAN) and the peroxypinopropionyl nitrate (PPN) are of importance for the radical chemistry in indoor air. Both radicals are present in photochemical smog, but can also be produced in indoor air as shown in Eqs. (6a)–(6c) for the formation of PAN from acetaldehyde.

\[ \text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O} \]  
(6a)

\[ \text{CH}_3\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO} + \text{M} \]  
(6b)

\[ \text{CH}_3\text{C}(\text{O})\text{OO} + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OONO}_2 + \text{M} \]  
(6c)

Jakobi and Fabian (1997) have measured PAN peak concentrations of 0.6–0.7 ppb (3–4 μg m⁻³) in indoor air during summer. Indoor related gas-phase chemistry of nitrogen-containing compounds has been reported by Atkinson et al. (1995b). Chandramouli et al. (2003) have postulated an influence of heterogeneous acid-catalyzed reactions of VOCs on aerosols.

The impact of VOCs and reactive gases on cultural objects is an important topic in museum research, which has been investigated intensively (Ankersmit et al., 2005; Hatchfield, 2002). However, this special part of indoor chemistry will not be discussed here.

3.2. Oxidation reactions of terpenes

Organic substances with an isoprenic structure like α-pinene, β-pinene, limonene, 3-carene, phellandrene, camphene, myrcene, ocimene, longifolene,
caryophyllene and others have been well described in indoor air. Terpenes belong to the class of biogenic hydrocarbons, which are ingredients of essential oils and are produced and emitted by living sources like plants. Common sources in indoor air are solvents of “green” or “eco” lacquers (turpentine balsam), softwood (Risholm-Sundman et al., 1998), air fresheners, personal care products and cleaning products (Salthammer, 1999). Singer et al. (2006a, b) and Destaillats et al. (2006) have shown that the use of some consumer cleaning agents can result in high levels of terpenes and terpene alcohols. Emission studies on freshly produced wooden shelf boards (untreated pine) and oriented strand board (OSB) yielded very high emission rates for α-pinene and 3-carene, respectively (Salthammer and Fuhrmann, 1996; Salthammer et al., 2003a).

Jann et al. (1997) have investigated eco-lacquers applied on pine boards in test chambers and have measured high limonene values. In addition, α-pinene, 3-carene and carvone were monitored in significant concentrations. Carvone (p-mentha-6,8-diene-2-one) is an interesting compound, because it is an ingredient of turpentine balsam but also an oxidation product of limonene. Monoterpenes are known as highly reactive with oxidizing agents like the hydroxyl radical and ozone in the atmosphere (Finlayson-Pitts and Pitts, 2000). The reaction with ozone seems to be a major pathway of degradation and various ozonolysis products have been described (Grosjean et al., 1993, Calogirou et al., 1999; Berndt et al., 2003; Wells, 2005). Weschler and Shields (1996, 1997) as well as Wolkoff et al. (1997) have mentioned that reactions of terpenes with ozone and/or hydroxyl radicals in indoor air may have significant impact on indoor air quality.

Although terpenes are highly reactive with the hydroxyl radical, it seems that most oxidation products in indoor air are produced by reaction with ozone in the dark. According to Eqs. (5a–5c), the reaction mechanism involves electrophilic addition on the –C=–C– bond, followed by decomposition into two carbonyl compounds and two Crigee-radicals. Estimated half-lives of α-pinene, β-pinene and limonene in the presence of 50 ppb (98 μg m⁻³) ozone are 1.81, 1.04 and 0.78 h, respectively (rate constants were taken from Finlayson-Pitts and Pitts (2000)). A typical product of ozone cleavage of limonene, which is one of the most important monoterpenes in indoor air, is 4-acetyl-1-methyclohexene (Manahan, 1994). Zhang et al. (1994a) have observed the formation of formic acid and acetic acid for the gas-phase reaction of limonene with ozone. Gas-phase reactions of ozone or NOₓ with terpenes and other unsaturated hydrocarbons have also been identified as sources of indoor particles (Weschler and Shields, 1999; Kamens and Jaoui, 2001; Sarwar et al., 2003; Fan et al., 2005). The influence of air exchange rates on reactions among indoor pollutants and on particle formation has been studied by Weschler and Shields (2000, 2003).

Clausen et al. (2001) and Wolkoff et al. (2000) have evaluated the airway irritation of a reaction mixture of R-(+)-limonene and ozone by a mouse bioassay. Klenø and Wolkoff, (2004) and Klenø Nøjgaard et al. (2005) have studied the effect on the human eye blink frequency of exposure to limonene and isoprene oxidation products. The human subjects were exposed to mixtures of terpenes with O₃, NO₂ and/or NOₓ. Changes of the blink frequency were attributed to low concentrations of irritants formed from gas-phase reactions. Hiramatsu and Miyazaki (2001; 2004) have investigated the effect of volatile matter from different species of wood chips and from softwood veneers on the activity of house dust mites and on the sensory evaluation of humans. The observed effect of dust mite activity suppression was strongly dependent on the type of wood and on the time of exposure. However, no negative effect on human comfort was measured. Tamas et al. (2006) have reported that ozone–limonene reactions influence the perceived air quality. In Germany, indoor air guideline values have been derived for bicyclic terpenes from available toxicological data (Sagunski and Heinzow, 2003).

3.3. Emissions from indoor-related products in the presence of ozone

Only little work is known about reactions of ozone with ingredients of building materials and about the decay rates of ozone in indoor air. Weschler et al. (1992) have measured VOCs in a freshly carpeted stainless-steel chamber in the presence of ozone (60–100 μg m⁻³). The gas-phase concentrations of styrene, 4-VCH and 4-PCH significantly decreased, while the concentrations of aldehydes (C₁–C₁₀) increased. Furthermore, the total concentrations of VOCs also increased markedly. The additional VOCs appeared to have been generated by reactions between ozone and non-volatile compounds associated with the carpets.
Secondary emissions of aldehydes from ozone interaction with carpet were also studied by Morrison and Nazaroff (2002). The heterogeneous chemistry of ozone on interior latex paint was investigated in a flow reactor by Reiss et al. (1995b). Formaldehyde was found to be produced by reactions related to the ozone concentration. The formaldehyde production was sufficient enough to impact indoor concentrations measurably. There was some evidence that acetaldehyde and acetone were also formed during ozone exposures. Moriske et al. (1998) have studied the influence of different building materials (wallpaper, latex paint, carpet, plywood and plaster) on the degradation of ozone in test chambers and in a model house. In the presence of single materials the decay was fast, resulting from a chemical reaction channel in addition to air exchange and physical sinks. Typically, the decrease of ozone concentrations to outdoor background values took 60–90 min. For all building materials, the formaldehyde concentrations were \(< 30 \mu g m^{-3}\) in the absence of ozone. In most cases the formaldehyde values increased significantly after charging the chamber with approx. 140 \(\mu g m^{-3}\) ozone. The highest detected formaldehyde concentration was 148 \(\mu g m^{-3}\). All cited studies demonstrate that formaldehyde seems to be one of the main products of ozone–alkene reactions. Knudsen et al. (2003) have evaluated the effect on perceived air quality from the interaction of ozone with eight different building products in test chambers and have seen distinct differences depending on the type of product. The exposure to primary and secondary air pollutants from cleaning products and air fresheners has been reviewed by Nazaroff and Weschler (2004).

3.4. Degradation of unsaturated fatty acids

Saturated and unsaturated aliphatic aldehydes are highly odorous and the odor impression is generally regarded as unpleasant. Common sources in indoor air are fatty acids like linoleic acid, linolenic acid (see Eq. (7)) and oleic acid, which are ingredients of many building products like wood, linoleum (Jensen et al., 1995a, b) and furniture coatings containing alkyd or natural resins (Afshari et al., 2003; Salthammer, 1997; Salthammer et al., 1999). On oxidation, many types of volatile aldehydes are formed. Typical degradation products of oleic acid are saturated aldehydes from heptanal to decanal, while linoleic acid gives mainly hexanal. Oxidation of linolenic acid leads to unsaturated compounds like 2,4-heptadienal (Belitz and Grosch, 1992). Zhang and Lioy (1994) as well as Zhang et al. (1994b) have studied indoor and outdoor concentrations of aldehydes and ozone in six residential houses. The study provided evidence that indoor ozone chemistry plays a role in generating acetaldehyde and hexanal. Furthermore, a rough correlation between formation of aldehydes and acids to the indoor ozone concentration was evident. Chamber tests carried out on wood and wood-based products showed that in addition to the wood species pine and the drying process (Manninen et al., 2002), the pressing process (Baumann et al., 1999, 2000; Jiang et al., 2002) is particularly responsible for the later release of VOCs. Freshly manufactured OSBs made of pine strands show besides the emission of monoterpenes also a considerable emission of pentanal, hexanal, heptanal, octanal and nonanal. These compounds are generated by thermal and oxidative degradation processes of wood chips during the drying process and then during the pressing process in the surface layers of the OSB (Salthammer et al., 2003a). Hodgson et al. (2002) have measured elevated concentrations of aliphatic aldehydes and terpenes in new manufactured houses with high surface ratio of wood products indoors.

\[
\begin{align*}
\text{Oxidation of linolenic acid leads to unsaturated compounds like 2,4-heptadienal (Belitz and Grosch, 1992). Zhang and Lioy (1994) as well as Zhang et al. (1994b) have studied indoor and outdoor concentrations of aldehydes and ozone in six residential houses. The study provided evidence that indoor ozone chemistry plays a role in generating acetaldehyde and hexanal. Furthermore, a rough correlation between formation of aldehydes and acids to the indoor ozone concentration was evident. Chamber tests carried out on wood and wood-based products showed that in addition to the wood species pine and the drying process (Manninen et al., 2002), the pressing process (Baumann et al., 1999, 2000; Jiang et al., 2002) is particularly responsible for the later release of VOCs. Freshly manufactured OSBs made of pine strands show besides the emission of monoterpenes also a considerable emission of pentanal, hexanal, heptanal, octanal and nonanal. These compounds are generated by thermal and oxidative degradation processes of wood chips during the drying process and then during the pressing process in the surface layers of the OSB (Salthammer et al., 2003a). Hodgson et al. (2002) have measured elevated concentrations of aliphatic aldehydes and terpenes in new manufactured houses with high surface ratio of wood products indoors.}
\end{align*}
\]

3.5. Degradation of cellulose

Horn et al. (1998) have reported high emissions of furfural and acetic acid from composite cork products. From chamber experiments it was concluded that furfural is not a native constituent of untreated natural cork or granulated cork. Both substances are produced under thermal stress from degradation of polyoses (hemicelluloses). Other degradation products are formic acid and hydroxymethylfurfural (Salthammer and Fuhrmann, 2000). Acetic acid results from elimination of acetyl-groups, while furfural is formed from pentoses and hexoses under elimination of water as
shown in Eq. (8) (Fengel and Wegener, 1989).

\[
\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{H} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

(8)

Substantial emissions of acetic acid and/or furfural could also be observed for heat-treated wood (“thermowood”) or kiln-dried samples of various wood species (e.g. beech, rubber wood, etc.). The degradation of hemicelluloses is acid-catalyzed, so in case of heat-treated wood-based building materials the process appears to be almost auto-catalyzed by the amounts of acetic acid generated. In Table 4, the results of a chamber test with UV-coated cork applied on concrete are shown (see table captions for experimental details). The high concentrations of acetic acid and furfural result from the manufacturing conditions. Other detected compounds will be discussed later on.

3.6. Light as a cause for secondary emissions

In many countries, legal requirements regarding the consumption and release of volatile solvents have encouraged manufacturers of coating systems to introduce more and more UV-curable formulations (Garratt, 1996). The technique reduces the amount of solvents required for the coating of metal, wood or other materials significantly and can even be utilized for powder-based systems. Photoinitiators start the curing process and are essential ingredients of UV-curable coating systems. However, photoinitiators are usually overdosed to avoid undercuring of the lacquer film and a certain amount of residual photoinitiator is left in the finished product after curing. The photochemistry of most common photoinitiators is a chemistry of the carbonyl group. The three important fragmentation processes forming radical species are Norrish I reaction (\(z\)-cleavage), Norrish II reaction and electron transfer. More detailed information about fragmentation processes of photoinitiators can be obtained from Fouassier (1995) and Crivello and Dietliker (1998). Fragmentation processes of photoinitiators form a number of volatile products, which may contribute to indoor air pollution. Benzaldehyde and alkyl-substituted benzaldehydes are usual components, because Norrish I is the most important reaction for cleavage. A well-known example is 1-phenyl-2-hydroxy-2-methyl-propane-1-one (PHMP). \(z\)-Cleavage generates two radicals in the first step. The benzoyl radical may recombine to benzil, reduction of PHMP leads to 1-phenyl-2-methyl-1,2-propane and acetone, recombination of the 2-hydroxy-propyl radical gives 2,3-dimethyl-2,3-butanediol (pinacol). Cyclohexanone is formed from the hydroxy–cyclohexyl radical upon \(\alpha\)-cleavage of 1-hydroxy-cyclohexyl-phenone (HCPK), followed by hydrogen abstraction and keto-enol-tautomerization as shown in Eq. (9). Photoinitiator fragments may reach considerable concentrations in indoor air. Typical time vs. concentration curves for the emission of benzaldehyde from three chamber tests carried out under different climatic conditions of a UV-cured furniture coating applied

<table>
<thead>
<tr>
<th>Compound</th>
<th>24 h</th>
<th>168 h</th>
<th>576 h</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg (h (m^{-2}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS2</td>
<td>3</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>Degradation of additive (adhesive)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>640</td>
<td>189</td>
<td>67</td>
<td>Degradation of hemicellulose</td>
</tr>
<tr>
<td>Furfural</td>
<td>203</td>
<td>43</td>
<td>31</td>
<td>Degradation of hemicellulose</td>
</tr>
<tr>
<td>Styrene</td>
<td>3</td>
<td>2</td>
<td>&lt; 1</td>
<td>Monomer</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>Degradation of photoinitiator</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>4</td>
<td>3</td>
<td>7</td>
<td>Degradation of photoinitiator</td>
</tr>
<tr>
<td>Phenol</td>
<td>2044</td>
<td>729</td>
<td>276</td>
<td>Cork binder</td>
</tr>
<tr>
<td>Methylbenzoate</td>
<td>8</td>
<td>2</td>
<td>&lt; 1</td>
<td>Degradation of photoinitiator</td>
</tr>
<tr>
<td>4-Phenylcyclohexene</td>
<td>13</td>
<td>2</td>
<td>1</td>
<td>Diels–Alder product</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>136</td>
<td>219</td>
<td>189</td>
<td>Photoinitiator</td>
</tr>
<tr>
<td>Sum of other VOCs</td>
<td>216</td>
<td>42</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

Test parameters: \(T = 23^\circ C\), r.h. = 45%, \(n = 1.0 \text{ h}^{-1}\), \(L = 1.0 \text{ m}^2\text{m}^{-3}\).
on wood are presented in Fig. 2. The influence of test conditions (see figure captions) is clearly visible and demonstrates the “post-curing” of the lacquer film if the surface is irradiated with typical daylight (Salthammer et al., 2002). Combinations of benzophenone and tertiary amines are used to form radicals via an excited electron transfer complex (exciplex). The photoproducts presented in Table 4 result from the blend HCPK/benzophenone used in the UV-lacquer. It should be mentioned that some photoinitiator fragments like benzaldehyde and acetophenone are typical degradation products of the polymeric Tenax TA (see Section 9).

\[
\begin{align*}
&\begin{array}{c}
\text{O} \\
\text{H}
\end{array} \\
&\begin{array}{c}
\text{O} \\
\text{H}
\end{array} \\
&\begin{array}{c}
+ \\
\text{OH}
\end{array}
\end{align*}
\]

Apart from the release of secondary emissions the presence of photoinitiators and uncured monomers in surface coatings may cause adverse effects, e.g. skin irritation and dermal burns upon contact with the film. Another undesired effect is a rapid yellowing of the surface.

Nowadays, the reduction of indoor air pollutants by photocatalysis has received considerable interest. Typical building products like wall paints are equipped with modified TiO\(_2\) to produce OH radicals and the superoxide radical ion O\(_2^-\) and act as a catalyst under indoor daylight conditions (> 400 nm). In chamber experiments it was shown that the method works well for nitrogen dioxide (NO\(_2\)) under dynamic conditions and for formaldehyde under static conditions. When the chamber was spiked with VOCs under dynamic conditions, no significant effect could be observed (Salthammer et al., 2006). So far, the method of photocatalysis was mainly applied by use of special flow reactors under UV light of high intensity, where high efficiencies could be found for different types of pollutants (Ao et al., 2003; Ao and Lee, 2004; Jo and Park, 2004; Yu et al., 2006). However, the reliability of photocatalysis for purification of indoor air has to be studied in detail, because oxidation products with negative impact on human health might be formed by typical indoor chemistry.

4. Hydrolysis as a cause for secondary emissions

4.1. Hydrolysis of esters

Depending on the moisture content of a product or the relative humidity in the indoor environment organic esters can hydrolyze to carboxylic acids and alcohols. The efficiency of the reaction also depends...
on other influences (temperature, pH value of the material) as well as on the type of ester.

Secondary emission of hydrolysis products can often be found where noticeable amounts of soft PVC are present in an environment (floor coverings, shower curtains, etc.). The plasticizers present in such products (phthalates, adipates) tend to hydrolyze over time. Typical reaction products found in indoor air samples are 2-ethyl-1-hexanol (hydrolysis of diethylhexylphthalate—DEHP) or n-/2-butanol (hydrolysis of di-/iso-butylphthalate—DBP/DIBP). Both substances are odorous compounds and may adversely influence the perceived air quality in that environment. Fang et al. (1999) as well as Wolkoff (1998) have reported that temperature and humidity have a strong impact on the chemical and sensory emissions from building products.

Odor nuisance due to 2-ethyl-1-hexanol emissions can become quite serious if PVC flooring material is glued to concrete slab that is not sufficiently dried—further drying of the slab is prevented by the diffusion barrier of the PVC, and the combination of readily available moisture in the material and the high pH of the concrete are perfect conditions for the hydrolysis of phthalate and adipate plasticizers in the material. From the high-boiling solvent 2-ethylhexylacetate, 2-ethyl-1-hexanol and acetic acid can be formed by hydrolysis under indoor conditions (see Eq. (10)). n-butanol is also a typical decomposition product of n-butylacrylate, which is used as a monofunctional monomer in adhesives and coatings. In Table 5, the results (secondary emissions) of a 1 m³ chamber test for a birch parquet coated with acrylic lacquer and applied on concrete are shown (see table captions for test conditions). The high concentrations of n-butylacrylate and n-butanol are obvious. The emissions of aliphatic aldehydes result from oxidation of fatty acids in the wood. The migration of 1-butanol and 2-ethyl-1-hexanol in composite flooring structures was studied by Sjöberg (2000).

4.2. Hydrolysis of organophosphate esters

Another example for the release of volatile products from rather non-volatile precursors is the release of halogenated compounds from phosphorous—organic flame retardants. 1-chloro-2-propanol, 2-chloro-1-propanol and 1,3-dichloro-2-propanol (see Eq. (11)) can appear in indoor air samples from hydrolysis of the common flame retardants tri(chloropropyl)phosphate (TCPP) and tris(dichloropropyl)phosphate (TDCPP), respectively (Salthammer et al., 2003b). The latter requires increased attention since 1,3-dichloro-2-propanol has been acknowledged as a carcinogenic substance.

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\text{O} \quad \text{O} \quad \text{P} \\
\text{O} \quad \text{O} \quad \text{P} \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\text{OH} + \text{H}_2\text{O} \\
(11)
\]

Table 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>24 h</th>
<th>168 h</th>
<th>720 h</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butanol</td>
<td>823</td>
<td>710</td>
<td>202</td>
<td>Hydrolysis of n-butylacrylate</td>
</tr>
<tr>
<td>Pentanal</td>
<td>30</td>
<td>33</td>
<td>7</td>
<td>Degradation of fatty acids (birch)</td>
</tr>
<tr>
<td>Hexanal</td>
<td>347</td>
<td>491</td>
<td>169</td>
<td>Degradation of fatty acids (birch)</td>
</tr>
<tr>
<td>n-butylacrylate</td>
<td>389</td>
<td>538</td>
<td>161</td>
<td>Monomer</td>
</tr>
<tr>
<td>Sum of other VOCs</td>
<td>864</td>
<td>289</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>

Test parameters: \( T = 23 \, ^\circ \text{C}, \, \text{r.h.} = 45\% , \, n = 0.4 \, \text{h}^{-1}, \, L = 0.4 \, \text{m}^2 \, \text{m}^{-3} \).
Other alcohols that are often found as hydrolysis products from flame retardants include 2-chloroethanol from tris(chloroethyl)phosphate (TCEP), 1-bromo-2-propanol, 2-bromo-1-propanol and 2,3-dibromo-1-propanol from tris(bromopropyl)phosphate (TBPP) and tris(dibromopropyl)phosphate (TDBPP), respectively. Rudel et al. (2003) have identified 2,3-dibromo-1-propanol in house dust and indoor air. Halogenated and non-halogenated phosphorous–organic flame retardants are used in hard foam, flexible foam, construction foam and other products made of polyurethanes. In case of fire-protected insulation foam, degradation products like 1-chloropropane and 1,2-dichloropropane could be identified (Salthammer et al., 2003b).

4.3. Hydrolysis of urea

A completely different indoor contamination source is glue based on urea-formaldehyde (UF) condensates. Such glues are utilized for the production of many kinds of wood-based material (particle boards, medium density fiber boards, high-density fiber boards and various natural fiber composites). The stability of these UF polymers against water is low. Therefore, the presence of the unavoidable amounts of water leads to a hydrolysis of the N–O bond and, as a consequence, to the release of formaldehyde. Since UF glues are commonly used in the manufacture of both building materials and furniture the loading factor of such products can be quite high in housings and offices. Especially the application of water-based flooring adhesives on UF-bonded particleboard may cause high and long-term emissions of formaldehyde.

\[
\text{NH}_2\text{NH}_2 + \text{H}_2\text{CO} \rightleftharpoons \text{H}_2\text{NCONH} + \text{H}_2\text{O} \tag{12}
\]

\[
\text{H}_2\text{NCONH}_2 + \text{H}_2\text{NCONH}_2 \rightleftharpoons 2\text{H}_2\text{NCONH} + \text{H}_2\text{O} \tag{13}
\]

The first two steps of the reversible urea–formaldehyde reaction are shown in Eqs. (12) and (13).

Phenol–formaldehyde resins are known to be stable against hydrolysis. However, some cork products are known as strong sources of phenol (see Table 4). In this case the high emission value results from an incomplete curing process during production.

5. Production conditions as source of emissions

If the production of a material utilizes extreme conditions (heat, moisture, chemicals) degradation processes can be started in the material. An example already mentioned is the thermal treatment of softwood strands during production of oriented strand boards (OSB). Especially the drying and pressing can involve temperatures high above 200 °C, which start degradation processes in the wood (see Sections 3.4 and 3.5). Strong emissions of acetic acid, hexanal and other aldehydes are the consequence. The release of those compounds can continue for months after production. In Fig. 3, the results of chamber tests with wood chips (wet, dried) and OSB (non-polished, surface-polished) are shown. The increase of aldehyde emissions after drying, pressing and polishing are obvious (see figure captions for test conditions).

Very remarkable substances can be formed during the production of styrene–butadiene-copolymers (SBR), which are used as foam backs for carpets. The reaction is a radical-induced polymerization. The residual monomers styrene and butadiene are removed by distillation, but the odor-intensive compounds 4-phenylcyclohexene (4-PCH) (from styrene and cis-butadiene, see Eq. (14)) and 4-vinylcyclohexene (4-VCH) (from cis- and trans-butadiene, see Eq. (15)) can be formed from the remaining monomers under the conditions of a thermally permitted \(\pi_4^s + \pi_2^s\) Diels–Alder cyclic addition (Fleming, 1976). 4-PCH is mainly responsible for the “new carpet smell” (Sollinger et al., 1993) and can be detected by the human nose in concentrations of only few \(\mu\text{g m}^{-3}\).

\[
\text{Ph} + \text{CH}_2 = \text{CH}_2 \rightarrow \text{PhCHCH}_2\text{CH}_2\text{Ph} \tag{14}
\]
Due to the reduced volatility of the substances and their formation in the depths of the material the emissions can continue for several weeks at the customer’s site. During indoor air studies carried out in six different office rooms three days after new carpets were laid, concentrations of 4-PCH in the range from 29–45 \( \mu \text{g/m}^3 \) were measured (Packebusch and Pluschke, 1993).

Another type of a \( \pi_4s^+\pi_2s^+ \) Diels–Alder reaction in a building product is the dimerization of 2-chloro-1,3-butadiene, which is used for the production of synthetic rubber. Due to the substituent in 2-position, the two different isomers 1-chloro-4-(1-chlorovinyl)-cyclohexene and 1-chloro-5-(1-chlorovinyl)-cyclohexene can be identified (Uhde, 2006).

Zn-diethyldithiocarbamate (ZDEC) is used as a vulcanization accelerator for the production of styrene–butadiene rubber (SBR). During polymerization ZDEC decomposes to carbon disulfide (CS\(_2\)) and diethylamine (see Eq. (16)). From diethylamine the carcinogenic compound N-nitrosodiethylamine can be formed from the reaction with NO\(_x\). In Table 6, the results of a chamber test with an SBR-adhesive applied on glass are shown (see table captions for experimental details). The high chamber concentrations of diethylamine, 4-PCH and 4-VCH clearly demonstrate the effect of the chemical reactions on the emission profile.

Azodicarbonamide decomposes at a temperature of about 200°C under formation of nitrogen (N\(_2\)) and is therefore used as a blowing agent in plastics industry. Semicarbazide (SEM) is another degradation product (see Eq. (17)) and the WHO has considered possible public health concerns with regard to SEM. In the indoor environment, SEM can be found in low concentrations in some types of plastics material.

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However, the compound is of very low volatility and could not be determined in indoor air.

\[
\begin{align*}
\text{H}_2\text{N} \quad \text{N} & \quad \text{O} \quad \text{N} \quad \text{H}_2\text{N} \\
\rightarrow & \\
\text{H}_2\text{N} \quad \text{N} & \quad \text{O} \quad \text{N} \quad \text{H}_2\text{N}
\end{align*}
\]  

(17)

6. Inter-species reactions

When two or more different kinds of material are fixed together, a variety of in-material reactions leading to VOC emissions are possible. The hydrolysis of esters fixed on wet concrete has already been discussed. In some cases such inter-species reaction may produce “exotic” compounds. A good example is the appearance of 1,6-dioxa-cyclododecan-7,12-dione, which emitted from a mouse pad. Adipinic acid was a component of the decorative layer, 1,4-butanediol was an ingredient of the adhesive and the carrier was made of PU foam. The reaction is a simple cyclization under elimination of water (see Eq. (18)).

\[
\begin{align*}
\text{H}_2\text{N} \quad \text{N} & \quad \text{O} \quad \text{N} \quad \text{H}_2\text{N} \\
\rightarrow & \\
\text{H}_2\text{N} \quad \text{N} & \quad \text{O} \quad \text{N} \quad \text{H}_2\text{N}
\end{align*}
\]  

(18)

During the test of a “green” paint the formation of dimethylformamide (DMF) from dimethylaminoethanol and formic acid was observed (suggested reaction see Eq. (19)). While dimethylaminoethanol (and probably traces of dimethylamine) were intentionally present in the paint, the formic acid (together with other carboxylic acids) was generated during the curing process of the lacquer film. Several micrograms of DMF per cubic meter air could be detected after 24h hours of drying/curing in the chamber. The appearance of DMF may cause problems in case of product ranking or labeling because of its classification as a toxic compound.

\[
\begin{align*}
\text{CO} & \quad \text{CH}_2 \quad \text{CO} \\
+ & \\
\text{HO} \quad \text{CH}_2 \quad \text{OH} \\
\rightarrow & \\
\text{CO} & \quad \text{CH}_2 \quad \text{CO}
\end{align*}
\]  

(18)

7. Metabolic reactions

The formation of metabolites from biological materials has been reported in detail. Fiedler et al. (2001) have identified about 150 MVOCs (microbial-originated VOCs) from 12 types of mold. However, in very few cases building products are directly involved. Gustafsson (1992) has reported relevant concentrations of highly odorous o-aminooacetophenone indoors. This compound is formed by degradation of the amino acid l-tryptophane, which is produced by an enzymatic reaction from the protein casein (see Eq. (20)). The latter is a component of casein glue and paint, which are still used for the restoration of cultural objects (Mills and White, 1994). Odor problems in museums have been reported due to degradation of casein to o-aminoacetophenone.

\[
\begin{align*}
\text{N} & \quad \text{H} \quad \text{NH}_2 \\
\text{O} & \quad \text{O} \\
\rightarrow & \\
\text{O} & \quad \text{O}
\end{align*}
\]  

(20)

Individual cases of complaints about musty odors in frame houses were noticed in the mid-1990s. The first component which could be clearly identified to be associated with the odor was 2,3,4,6-tetrachloroanisole (Gunschera et al., 2004). This brought up the question of its origin, because chloroanisoles have never been produced on an industrial scale, especially not for use with building materials. On the other hand, chloroanisoles are well known as metabolites of chlorinated phenols (Ide et al. 1972; Pfeifer and Ballschmiter, 2002; Rott et al., 1979). All of the affected houses from which chloroanisoles have been identified were in coincidence with the application of pentachlorophenol (PCP). In the 1960s and 1970s, PCP treatment was commonly used in Germany to protect building products made of wood against decomposition by fungi. Technical PCP has a purity of about 90% and is contaminated with other chlorinated phenols, especially 2,3,4,6-tetrachlorophenol (WHO 1987). Also the latter compound can be formed by microbial dechlorination of PCP. Furthermore, it can be methylated to 2,3,4,6-tetrachloroanisole by microorganisms (see Eq. (21)). Local dampness probably favours microbial growth associated with metabolic conversion of chlorophenols to the corresponding
chloroanisoles, primarily 2,3,4,6-tetrachloroanisol, which spread throughout the buildings, resulting in the observed odors. Chaetomium and Penicillium species have been identified which are responsible for the chloroanisole formation (Gunschera et al., 2005).

8. Miscellaneous

2,4,7,9-tetramethyl-5-dicyne-4,7-diol (T4MDD), is used as a wetting and defoaming agent in several water-based lacquer systems. During a chamber study of a coating system for wood-based furniture, two unexpected components appeared in the chamber air, which could be identified as 4-methyl-2-pentanone (MIBK) and 3,5-dimethyl-1-hexyne-3-ol (Salthammer et al., 1999). Analysis of the coating material and comparison experiments using pure T4MDD yielded, that both compounds are formed by decomposition of T4MDD as shown in Eq. (22). Wells (2004) has recently studied the decomposition of T4MDD in the gas phase.

9. Analytical artifacts caused by chemical reactions

In some cases, chemical reactions may occur under the conditions of the analytical procedure and pretend the presence of indoor pollutants. For air sampling the adsorbent Tenax TA is frequently used. Compounds like benzene, benzaldehyde, acetophenone and benzoic acid may appear as blank readings from the thermal treatment of Tenax TA. Clausen and Wolkoff (1997) have shown that Tenax TA decomposes in the presence of NOx. Klenø et al. (2002) have identified a total of 25 Tenax degradation products from sampling of NO, NO2, O3, H2O2, OH and limonene-O3 mixtures. A known artifact in gas-chromatographic analysis is the formation of 1,1-dimethoxy-cyclohexane from cyclohexanone in methanolic standard solutions. Careful analysis is required to avoid misinterpretation of such undesired effects.

10. Conclusions

A trend to reduce or remove certain volatile compounds (e.g. aromatics, halogenated hydrocarbons) from building products and consumer goods has started many years ago and has lead to a certain decrease in VOC emissions. However, the number of chemicals present in building materials is still increasing. Many products commonly used indoors emit reactive compounds or secondary products due to their composition or to the manufacturing process. Some important examples are given in Table 1 but it is expected that many more types of reaction and species could be detected in the indoor environment. It was already mentioned that reactive compounds and reaction products can have a negative influence on human well-being even at low concentrations due their odor intensity, their irritant effect or their potential for particle formation. It is therefore essential to take into consideration the aspect of “Indoor Chemistry” in the chemical characterization of indoor air. Furthermore, the testing of single products under standard conditions may help to reduce VOC/SVOC emissions but does not appear to give realistic results.
Depending on the product type it seems more desirable to select those conditions that can stimulate possible chemical reactions and therefore the release of secondary products in order to determine the true usability of the products. It is our opinion that the problem with secondary emissions from building materials will probably increase in the future. Unsaturated hydrocarbons like terpenes are increasingly found in the indoor environment due to more natural/recycled building materials, odorants, etc. and ozone levels can be quite high indoors. It is therefore likely that the number of complaints due to such emissions will be higher than today’s complaints about primary emissions. The indoor environment is a complex field and so is indoor chemistry. We are far away from a complete understanding of chemical reactions among indoor pollutants and their impact on human health. For a deeper insight multidisciplinary research at the interface between medical sciences and chemistry is needed.

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