Volatile organic compounds (VOCs) formation due to interactions between ozone and skin-oiled clothing: Measurements by extraction-analysis-reaction method

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Abstract

The reaction between ozone and human skin lipids/skin-oiled clothing has been recognized as an important source of volatile organic compounds (VOCs), especially aldehydes and ketones indoors. Existing research on this topic was mainly focused on VOC products measurement and factors influencing the reaction. Reactants were neglected in reaction analysis and quantity of reactants was not well controlled in comparative experiments. To overcome these disadvantages, a new method was proposed for investigation on reaction between ozone and skin-oiled clothing. The method included four procedures: extraction of skin-oiled clothing, analysis of the extracts, reaction between ozone and the extracts in environmental chamber, and analysis of relationship between VOC products and corresponding reactants. The profile of extracts from skin-oiled clothing, and ozone deposition velocity on clothing and molar yields of major VOC products in environmental chamber experiment agreed well with that of previous studies. Moreover, the possible primary precursors of four major VOC products, i.e. acetone, 6-methyl-5-hepten-2-one (6-MHO), nonanal and decanal, were inferred based on the profile of compounds from skin-oiled clothing and analysis of chemical structure. It indicated that the method proposed in this study can provide acceptable accuracy for studies about ozonation of skin-oiled clothing. This method is particularly appropriate when information of reactants or quantity control of reactants is required in reaction analysis and experiment.

1. Introduction

Ozone is recognized as an important gaseous pollutant which may lead to severe health problems. Exposure to ozone contributes to asthma and various respiratory symptoms [1–5], and symptoms related to eyes [6]. Previous studies have reported significant associations between increase in mortality and exposure to ambient ozone concentration [7,8]. The ambient ozone can be transported to indoor environment by ventilation and infiltration. Generally, the indoor ozone concentration is lower than that in the ambient due to ozone removal by indoor surfaces and indoor gas phase reactions. Even low ozone level indoors can still cause adverse influence on human health [9]. Moreover, indoor ozone-initiated chemistry can produce secondary emission of particulate matters [10] and volatile organic compounds (VOCs), such as aldehydes and ketones, which may be more harmful than ozone itself [11]. Hence, it is important to investigate the ozone gas phase and surface reaction indoors.

Humans can provide adequate sites for ozone-initiated chemistry [12] since ozone can react with human lipids on skin [13] and clothing [14], and generate VOCs. A field study by Guan et al. [15] detected 6-methyl-5-hepten-2-one (6-MHO), an indicator VOC product in ozonation of human lipids, in more than 50% of all 107 commercial flights measured. Gao et al. [16] estimated the contribution of human skin and ozone reaction on VOC concentration in aircraft cabins based on results of field test on five flights and concluded that the total VOC contribution could reach as much as 70%. Fischer et al. [17] implemented a real-life study in a classroom with 24 pupils and a teacher to investigate ozone removal by occupants and the rate of 4-oxopentanal (4-OPA) and 6-MHO produced. Their results indicated that humans in the presence of ozone gave rise to the target VOCs and the ozone removal caused by occupants was approximately 2.6 times larger than that of other...
available surfaces in such a densely occupied building. These field studies provided useful results on ozone removal and detection of VOC products in interaction between ozone and humans. However, detailed and quantitative analysis was not given due to complicated uncontrolled factors, such as temperature, humidity and human behaviors.

Some researchers conducted experiments in chambers with controlled environment and subjects to get detailed information on ozone reaction with humans. A study by Wisthaler and Weschler [13] showed that the presence of two adult individuals in a simulated office with ozone can lead to a considerable increase in acetone, 6-MHO, geranyl acetone, decanal, 4-OPA and 1,4-butanediol. Quantitative relation between ozone and prominent VOC products during ozonation of human lipids was obtained. Tamás et al. [18] analyzed factors affecting ozone removal in a cabin mockup of a B-767 airliner and found that occupants and clothing accounted for about 58% of ozone removal in cabin environment. Weschler et al. [19] monitored ozone and dominant VOC products, i.e. aldehydes and ketones, in an occupied simulated aircraft cabin and concluded that the products of ozone interactions with humans were responsible for more than half of the oxidation products identified in the cabin air. These studies took whole human body as investigation subjects while others focused on specific parts of humans. Coleman et al. [20] studied the ozone interaction with aircraft cabin materials and clothing fabric in a small-scale environmental chamber under different environment conditions. They concluded that soiled clothing contributed to ozone removal and VOC emissions dominantly in spaces with large population, and relative humidity in the chamber had significant influence on VOC formation in the ozonation of cabin materials and clothing. Rai et al. [21] performed a series of experiments in an 8 m³ chamber to study the ozone reaction with soiled clothing, and the effect of inlet ozone concentration, humidity, soiling level of clothing and air exchange rate on ozone removal and VOC emissions. Nevertheless, in above experiments, only the average VOC concentrations were measured and the time variation was neglected. Additionally, the quantities of reactants on the clothing were not well controlled in comparative experiments. Furthermore, the reactants that interacted with ozone and the products were not measured in the same experiments. Thus, the relationship between reactants and products cannot be well understood.

This study concerns both reactants and VOC products during ozonation of skin-oiled clothing. An extraction-analysis-reaction (EAR) method was first proposed. The components of a skin-oiled T-shirt were analyzed by gas chromatography-mass spectrometry (GC-MS) after extraction, rotary evaporation and derivation. Then the extracted liquid was painted on a piece of clean T-shirt, and reacted with ozone in a small scale chamber with moderate air exchange rate. The VOC products were measured hourly and the relationship with corresponding reactants was analyzed.

2. Materials and methods

2.1. The experimental method

The EAR method was developed mainly for two purposes: (i) to obtain the component information of skin-oiled clothing so that the reactants in ozonation can be explicit and the relationship with homologous products can be well understood; (ii) to control the quantity of reactants accurately when comparative experiments are needed. To achieve these goals, the EAR method included the following steps as shown in Fig. 1: (i) A clean T-shirt was worn by a volunteer to become skin-oiled. The skin-oiled clothing got extracted in methanol and concentrated by rotary evaporation. The final concentrated extracts, which were the essence of the method, were sealed and in cold storage. (ii) The sample of the concentrated extracts was analyzed by GC-MS to obtain the components profile, thus the reactants information in ozonation could be acquired. (iii) The sample of the concentrated extracts was painted on a clean clothing piece. Then the soiled clothing piece reacted with ozone in an environmental chamber with moderate air exchange rate and controlled temperature and humidity. The VOCs inside the chamber were measured, thus the VOC products information in ozonation could be acquired. (iv) Based on chemical structure analysis, the corresponding reactants of VOC products could be inferred.

2.2. Extraction of skin-oiled clothing

A cotton-polyester sleeveless T-shirt was washed in fragrance-and dye-free detergent, and dried by an air blower in a clean room. Then it got skin-oiled by a 21-year-old Chinese male subject who wore it for 14 h, including sleeping time. The soiled T-shirt was then immersed in 1L methanol in a glass bottle for extraction. During extraction, the glass bottle was sealed to avoid oxidation, and placed still in a water bath to keep at 30 °C. After extraction for 16 h, the extraction liquid was filtered and then rotary evaporated at room temperature and 0.09 MPa vacuum degrees until the liquid left was less than 100 mL. Vacuum condition could accelerate the evaporation process and preclude oxidation of the extracts. During the rotary evaporation, there were no precipitated phases in the liquid, indicating proper evaporation conditions and sufficient solvents. Afterwards, extracts were dissolved with methanol to 100 mL in a constant-volume bottle and stored in a refrigerator below 4 °C after being sealed. As comparison, a clean T-shirt from the same dozen was also washed, extracted, concentrated and stored without being skin-oiled to get the components of blank clothing.

2.3. Analysis of extract components

Component analysis of human skin lipids using high temperature GC-MS has been conducted by some researchers [22–25]. Generally, the analyzing process includes several procedures to pretreat samples rather than direct injection into GC-MS. In this study, an appropriate method for analyzing extract components was proposed after several trials.

200 μL extracts of skin-oiled clothing and blank clothing were taken out and derivatized with methanolic boron trifluoride, respectively. Then the derivatives were extracted with hexane in separating funnel to wait for layering stationary. Afterwards, the upper phase was dried under N2 flow and then resuspended in 200 μL hexane before injected into GC-MS. The derivatives were analyzed by an Agilent 7820A GC system (Agilent, Cork, Ireland) coupled with a 5975C MS with an Agilent HP-5MS 30 m × 0.25 mm (i.d.) × 0.25 μm capillary column. Carrier gas was high purity helium. One microliter was injected using Agilent G4513-7693 auto injector. The temperatures of injection port and ion source were 280 °C and 250 °C, respectively. The initial oven temperature of 100 °C was held for 2 min, raised to 300 °C at 10 °C min⁻1, and then held for 5 min (27 min in total). The GC was operated in the splitless mode, and the MS was operated in Scan (mass range 35–400 AMU) acquisition mode.

2.4. Reaction with ozone in environmental chamber

A 53L stainless environmental chamber, equipped with a water bath for controlling temperature in the chamber at 25 ± 0.5 °C, was used to conduct the experiment. The schematic of the experimental system is shown in Fig. 2. One night before each experiment, the chamber was cleaned by distilled water and methanol, and then
Fig. 1. Schematic showing the EAR method.

Fig. 2. Experimental system of reaction in an environmental chamber.
supplied with clean air by synthetic air cylinder at 0.88 L/min, i.e. 1 h⁻¹ air exchange rate, with the control of pressure reducing valve and flow controller. Before entering into the chamber, the clean air went through a humidity controller to control relative humidity in the chamber at 50 ± 5%. A thin glass tube under an ultra-violet (UV) lamp was used to generate ozone. Ozone monitor (Model 205, 2B Technology, USA) was placed at the outlet of the chamber to measure exhaust ozone concentration every 10 s till the end of experiment. In the experiment, the exhaust ozone concentration of empty chamber was controlled at 80 ppb according to the Chinese national standard [26], which could be regarded as the net inlet ozone concentration in the chamber during the experiment.

Pieces of 25 cm × 20 cm were cut from a dozen cotton-polyester T-shirts mentioned above, and washed by distilled water. After drying, the clothing pieces were exposed to ozone under the UV lamp overnight for elimination of possible residual reactants before the experiment so that the main reactants were from the extracts of skin-oiled clothing as mentioned below. At the beginning of the experiment, the ozonized clothing piece was soaked in 10 mL extracted liquid from skin-oiled T-shirt to absorb the extracts fully. The volume was determined in accordance with clothing piece area approximately: 10 mL for reaction from 100 mL total extraction while 0.05 m² clothing piece from 0.55 m² T-shirt. Then it was placed into the chamber. Note that all the steps concerning T-shirts and pieces mentioned above were operated with disposable gloves to avoid effect of lipid on hands. The environmental chamber was placed into the chamber. Note that all the steps concerning T-shirts and pieces mentioned above were operated with disposable gloves to avoid effect of lipid on hands. The environmental chamber was ventilated with 5–6 L/min N₂ flow for 30 min and then 0.88 L/min N₂ flow for another 30 min. The aim of this step was to evaporate residual methanol while preventing oxidation of extracts. The gas source was then switched to synthetic air cylinder and the settings were in accordance with that before the experiment (0.88 L/min with UV lamp on). After the chamber was supplied with synthetic air, VOC products were sampled hourly for 8 h. C6–C10 straight-chain saturated aldehydes, 6-MHO and other large-molecule gaseous products were collected by drawing exhaust air through the Tenax-TA tube using a sampling pump (QC-II, Beijing Municipal Institute of Labor Protection, China) at 400 mL/min for 20 min (i.e., with a sampling volume of 8 L). Then the Tenax-TA tubes were put into thermal-desorber (TD, Markes, Inc. UK), which injected the desorbed sample air into the GC (Model 6875, Agilent, USA), coupled with a MS (5975B, Agilent, USA) with an HP-VOC capillary (30.0 m × 200 μm × 0.1 μm film thickness). The initial temperature of the oven was 40 °C, and then increased up to 250 °C at 10 °C/min, held for 5 min. For detection of acetonitrile, acetonitrile samples were collected at a flow rate of 400 mL/min for 20 min through DNPH-coated silica cartridges (Cleanert, USA). After sample collection, each cartridge was eluted with 5 mL of acetonitrile. Then the eluent was analyzed by injecting 20 μL into an Agilent 1200 high performance liquid chromatography (HPLC) equipped with a photodiode detector operating at 360 nm and an Agilent SB-C18 reversed-phase column (250 mm × 4.6 mm, 5 μm). The mobile phase consisted of three solvent mixtures: mixture A, 50:20:50 (v/v/v) of acetonitrile/methanol/water; mixture B, 20:65:15 (v/v/v) of acetonitrile/methanol/water; mixture C, 25:65:10 (v/v/v) of acetonitrile/methanol/water. The gradient program was a linear gradient from 100% A to 100% B in 10 min, followed by a linear gradient from 100% B to 100% C in 4 min. The flow rate was 1.2 mL/min and the column temperature was 35 °C. Note that sampled air went through disposable ozone scrubbers before entering collectors (Tenax-TA tubes and DNPH-coated silica cartridges) and each sample was duplicated.

2.5. Formation inference of selected VOCs

Ozone reaction with human skin lipids was a complicated chemistry process. Several unsaturated compounds in skin lipids contain more than one unsaturated carbon–carbon bond, e.g. squalene. When these compounds interact with ozone, the products may be further reactive since ozone can attack residual unsaturated carbon–carbon bonds. Therefore, in the reaction between ozone and human skin lipids, both the reactants and products include primary and secondary ones [13]. In this study, only primary reactants and products were considered to avoid uncertainty of determination on secondary reactants and products. Specifically, acetone, 6-MHO, nonanal and decanal, and their corresponding primary precursors, i.e. the compounds detected on soiled clothing, were focused in this investigation.

Regularity of ozone attacking double carbon–carbon bonds is beneficial for analyzing relationship between reactants and corresponding products [27,28]. Fig. 3 illustrates the reaction process in ozonation of unsaturated carbon–carbon bond [29,30]. In both Path a and Path b, the products are expected to be carbonyls and the Criegee intermediates. The Criegee intermediate cannot exist steady but rearrange to a carboxylic acid or ester, or decompose to form stable products, such as CO₂ and free radicals. The carbonyls, especially aldehydes and ketones, are detectable and traceable for homologous precursors based on chemical structure analysis: comparing groups other than carbonyls of products with groups other than double carbon–carbon bonds of possible reactants. For instance, when decanal was selected to search for its precursors, the group R₁ and R₂ (or R₁ and R₂) should be H and straight-chain C₆H₁₂ respectively, which meant that the precursors of decanal should have a −H and a straight-chain −C₆H₁₂ connected to a carbon with a C=C bond. By ransacking and comparing group information of possible reactants with unsaturated carbon–carbon bonds, the precursors of selected VOC products can be determined.

3. Results and discussion

3.1. Composition of the extracts

GC-MS profile of extracts from skin-oiled T-shirt and blank T-shirt is shown in Fig. 4 by setting the abundance of squalene as 100%. Compounds from the skin-oiled T-shirt could be categorized into four: free fatty acids, squalene, cholesterol and other compounds. Free fatty acids, constituting for about 50% of all compounds detected, could be further classified into unsaturated ones, e.g. palmitoleic acid and oleic acid, and saturated ones, e.g. hexadecanoic acid and octadecanoic acid. Quantitatively, the unsaturated and saturated free fatty acids were similar, accounting for 51.5% and 48.5% of total free fatty acids respectively. Squalene was the most abundant component detected in the extracts, making up for more than 25%. Cholesterol appeared in the latter part of the profile, accounting for about 3.7%. The rest 20% other compounds consisted of hydrocarbons, esters and aromatic compounds. The information of major compounds detected is listed in Table 1 by class. Among these compounds categories, unsaturated free fatty acid and squalene were the main reactants in the interaction of skin lipid and ozone since they contained abundant unsaturated carbon–carbon bonds. In comparison, species and quantities of detected compounds from the blank clothing were much less than that of skin-oiled clothing. Squalene, cholesterol and most free fatty acids were not detected in extracts of blank clothing, indicating that the blank clothing was much less reactive than the skin-oiled one when reacting with ozone.

Table 1 shows that major compounds of free fatty acids were contained between C12 to C18. The most abundant compounds of saturated and unsaturated free fatty acids were hexadecanoic acid (C16:0) and 6-hexadecenoic acid (C16:1n6), respectively. Other plentiful saturated free fatty acids included, in order of abundance, tetradecanoic acid (C14:0), pentadecanoic acid (C15:0),...
Fig. 3. Scheme of ozone reaction with unsaturated carbon-carbon bond.

Fig. 4. GC-MS profile of extracts from skin-oiled and blank clothing. Solid line represents the skin-oiled clothing, while dash line represents the blank one. Y-axis represents ratio of the abundance of detected compounds and that of detected squalene from skin-oiled clothing.

Table 1
Major detected compounds of skin-oiled clothing in five categories and their relative abundance.

<table>
<thead>
<tr>
<th>Category</th>
<th>Formula</th>
<th>Compound name</th>
<th>Relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated free fatty acids</td>
<td>C16:0</td>
<td>Hexadecanoic acid</td>
<td>9.2%</td>
</tr>
<tr>
<td></td>
<td>C14:0</td>
<td>Tetradecanoic acid</td>
<td>5.4%</td>
</tr>
<tr>
<td></td>
<td>C15:0</td>
<td>Pentadecanoic acid</td>
<td>3.2%</td>
</tr>
<tr>
<td></td>
<td>C18:0</td>
<td>Octadecanoic acid</td>
<td>2.7%</td>
</tr>
<tr>
<td></td>
<td>C12:0</td>
<td>Dodecanoic acid</td>
<td>1.7%</td>
</tr>
<tr>
<td>Unsaturated free fatty acids</td>
<td>C16:1n6</td>
<td>6-Hexadecenoic acid</td>
<td>8.5%</td>
</tr>
<tr>
<td></td>
<td>C18:1n9</td>
<td>9-Octadecenoic acid</td>
<td>5.5%</td>
</tr>
<tr>
<td></td>
<td>C17:1n6</td>
<td>16-Heptadecenoic acid</td>
<td>1.9%</td>
</tr>
<tr>
<td></td>
<td>C15:1n14</td>
<td>14-Pentadecenoic acid</td>
<td>1.5%</td>
</tr>
<tr>
<td></td>
<td>C14:1n11</td>
<td>Z-11-Tetradecenoic acid</td>
<td>1.3%</td>
</tr>
<tr>
<td>Squalene</td>
<td>C30H50</td>
<td>Squalene</td>
<td>26.6%</td>
</tr>
<tr>
<td>Cholesterol</td>
<td>C27H46O</td>
<td>Cholesterol</td>
<td>3.7%</td>
</tr>
<tr>
<td>Other compounds</td>
<td>C13H20O2</td>
<td>Isoalantolactone</td>
<td>3.0%</td>
</tr>
<tr>
<td></td>
<td>C25H50</td>
<td>(4-octyldodecyl)-Cyclopentane</td>
<td>1.4%</td>
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</table>
octadecanoic acid (C18:0) and dodecanoic acid (C12:0). As for unsaturated free fatty acids, the secondary affluent compound was 9-octadecenoic acid (C18:1n9), followed by 16-heptadecenoic acid (C17:1n6), 14-pentadecenoic acid (C15:1n4) and Z-11-tetradecenoic acid (C14:1n11). This result was quite consistent with that detected by Ni Raghallaigh et al. [25] at major fatty acids. It is worth mentioning that the C16:1n6 shown in Table 1 might be a mixture of C16:1n6 and C16:1n9 since these two isomers were unable to be separated chromatographically. However, C16:1n6 has been proved to be more than 40 times abundant than C16:1n9 [31]. Therefore, it was reasonable to treat it as C16:1n6 [25].

When referring to previous studies about composition of skin lipids, there was an apparent difference with this study about relative abundance of major compounds. It seemed that relative abundance of compounds detected in this study was nearly twice that of same compounds in other investigations. For example, unesterified fatty acids, squalene and cholesterol accounted for about 25%, 12% and 2% respectively in literature [24,31], while the values in this study were 50%, 26.6% and 3.7% respectively. Since the highest oven temperature was 300 °C in the GC-MS, most waxes and triglycerides of large molecules were not detected, which constituted for about 50% of total compounds. Most unsaturated wax esters and triglycerides were synthesized by two or three groups contained between C13 to C22. Therefore, their reactive properties in ozonation were similar with that of unsaturated fatty acids. Thus, in our study, unsaturated wax esters and triglycerides were not considered. Despite some divergence with previous studies in relative abundance and detective range, the ratio between abundance of major compounds agreed well, shown in Table 2. It indicated that the method for extraction and analysis of components of skin-oiled clothing provided considerable accuracy and was acceptable for this study.

It was worth mentioning that methanol working as solvent for extraction of skin-oiled clothing would have several advantages in comparison with other solvents: (i) methanol was less evaporative and safer than methylene chloride; (ii) methanol would not contaminate sampling tubes, i.e. Tenax-TA tubes and DNPH-coated silica cartridges, while ether and hexane would be absorbed by Tenax-TA tubes and affect peaking of its surrounding compounds in GC-MS; (iii) methanol would help for methylation during extraction so that the separation of skin lipid compounds in GC-MS could be better. Thus, methanol can be a good solvent other than methylene chloride, ether and hexane for extraction of skin lipids in future studies.

### 3.2. Ozone and VOC products in chamber experiment

The concentrations of ozone and selected VOCs during the chamber experiment were presented in Fig. 5. Ozone concentration witnessed a sharp increase at the beginning of the experiment and achieved a steady state at 13 ppb from the 3rd hour. Since the exhaust ozone concentration of the empty chamber was 80 ppb, the ozone concentration reduction of 67 ppb attributed to ozone consumption of the soiled T-shirt piece in the chamber. The concentrations of selected VOCs shared similar trend with ozone: experiencing a significant growth in the 1st hour and growing gradually till remaining nearly constant from the 6th hour. Among the four selected VOCs, acetone was observed as the most abundant product, followed by decanal, while the final concentrations of 6-MHO and nonanal were approximately equivalent. Specifically, the acetone concentration increased more than 20 μg/m³ during the experiment. The concentration of decanal had a 14 μg/m³ net increase and the 6-MHO concentration increased more than 7.5 μg/m³ during the ozonation of the soiled clothing piece. About 6 μg/m³ nonanal were generated in the reaction of ozone and the soiled clothing piece.

To quantify the reaction process and compare with other studies, ozone deposition rate on the soiled clothing piece and molar yields of selected VOCs were calculated. These two parameters were used to describe ozone consumption by surfaces and VOCs formation quantitatively in the interaction of ozone and other reactive compounds. In this study, ozone deposition rate on clothing \( \nu_d \) was obtained by:

\[
\nu_d = \lambda \left( \frac{[O_3]_{\text{empty-ex}} - [O_3]_{\text{occupied-ex}}}{[O_3]_{\text{occupied-ex}}} \right) V_{\text{chamber}} A_{\text{clothing}}
\]

Where,

\( \lambda \): The air exchange rate of the ventilated chamber, 1 h⁻¹;
\([O_3]_{\text{empty-ex}}\): The exhaust ozone concentration of the empty chamber, 80 ppb;
\([O_3]_{\text{occupied-ex}}\): The exhaust ozone concentration of the chamber with soiled clothing piece inside, 13 ppb;
\( V_{\text{chamber}}\): The volume of the environmental chamber, 53 L;
\( A_{\text{clothing}}\): The area of the soiled clothing piece, 0.05 m².

The molar yield of VOCs, characterizing the conversion efficiency of ozone to VOCs, was defined as the moles of VOCs produced per mole of ozone consumed by a reacting surface [19]. It was attained by Equation (2) in this study:

\[
Y_1 = \frac{[\text{VOC}]_{\text{final}} - [\text{VOC}]_{\text{initial}}}{[O_3]_{\text{empty-ex}} - [O_3]_{\text{occupied-ex}}}
\]

Where,

\( Y_1 \): The molar yield of VOC;
\([\text{VOC}]_{\text{final}}\): The final amount of VOC in the chamber, mol;
\([\text{VOC}]_{\text{initial}}\): The initial amount of VOC in the chamber, mol;
\([O_3]_{\text{empty-ex}}\) and \([O_3]_{\text{occupied-ex}}\): Same meaning as in Equation (1) with the unit converted to mol.

Ozone deposition velocity on skin-oiled clothing and molar yields of selected VOCs computed in this study and reported in relevant literature are listed in Table 3 for comparison. The ozone deposition velocity in the literature was fairly consistent, ranging from 0.15 to 0.37 cm/s, while the value of this study was at bottom of the range. If comparing with results in similar environmental condition, i.e. 0.5 h⁻¹ air exchange rate, 49% relative humidity and 24 ppb exposure ozone concentration in Rai et al. [21], the result in our study was slightly smaller (0.15 ± 0.02 cm/s vs. 0.20 ± 0.02 cm/s). A possible reason was that the extraction process discarded human skin scurf and microbes adhering to clothing that might contribute to ozone consumption, which made the ozone deposition smaller in turn. As for molar yields of selected VOC products, the values from references were not consistent except for acetone and 6-MHO. The main range of molar yield of acetone was 8%–13%, and that of 6-MHO was 1%–3%. The results of this study, 11.8% ± 0.5% and 2.0% ± 0.3% respectively, agreed well with this range. The molar yields of decanal and nonanal were approximately

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Ratio of major compounds in references and this study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Reference</td>
</tr>
<tr>
<td>Free fatty acids/Squalene</td>
<td>2.08 [31]</td>
</tr>
<tr>
<td>Squalene/Cholesterol</td>
<td>7.00 [24]</td>
</tr>
<tr>
<td>C16:0/C16:1</td>
<td>1.03 [25]</td>
</tr>
</tbody>
</table>

* Data of skin lipids from subjects’ back.
in consistency with that of Weschler et al. [19] but smaller than that of Rai et al. [21]. The fairly good accordance with previous studies indicated that the experimental procedure, including extraction and reaction, could provide acceptable accuracy for investigation on interactions between ozone and skin-oiled clothing.

3.3. Relationship between selected VOC products and reactants

By the inference method mentioned in Section 2.5, we searched the detected compounds list of extracts from skin-oiled T-shirt and found possible primary precursors of selected VOC products, illustrated in Table 4 in order of molecular weight of VOC products and abundance of reactants. Note that the highest abundance of reactive compounds did not mean producing the largest amount of products necessarily, since the reaction process was greatly influenced by reaction probability with ozone.

The major primary precursors of acetone would be squalene, genaryl acetone and 2-methyl-2-docosene, of which squalene and genaryl acetone were also the main reactants that produced 6-MHO. The reason why these two compounds can generate different products was that ozone attacked double carbon-carbon bonds at different positions: acetone was the main VOC product when ozone attacked the first double carbon-carbon bond from the ends, while 6-MHO was the main one when ozone reacted with the second unsaturated bond from the ends. Fatty acids were the main precursors of nonanal and decanal. For nonanal, the dominant fatty acids as precursors were 9-octadecenoic acid and (Z)-7-hexadecenoic acid. (Z)-13-Docosenamide would contribute to generation of nonanal as well. As for formation of decanal, reaction between ozone and 6-hexadecenoic acid, the most abundant unsaturated fatty acid, would be the dominant cause. Meanwhile, ozonation of 8-octadecenoic acid would also lead to generation of decanal. Additionally, as mentioned before, unsaturated wax esters and triglycerides containing similar structure with these fatty acids would be precursors of nonanal and decanal as well. The inference of these precursors was not only in consistency with that by Wisthaler and Weschler [13], but also supplemented information of precursors for acetone and nonanal because of the fairly complete profile of compounds from skin-oiled clothing.

As emphasized in Section 2.5, only primary reactants and products were considered in this study. Secondary reactions can be very complicated. For example, products in ozonation of squalene can be C27-pentaenal, C22-tetraenal, C17-trienal, C27-pentaenoic acid and so on. These products can further react with ozone and generate acetone and 6-MHO [13]. In fact, 6-MHO can also be a secondary precursor for acetone: generating acetone and 4-OPA. When comparing with other studies [13,19], it can be inferred that there was secondary reaction between ozone and 6-MHO in our

Fig. 5. Time evolution of ozone and selected VOCs during the chamber experiment. Error bars indicate plus one standard deviation from analysis of duplicated samples.

Table 3

<table>
<thead>
<tr>
<th>Studies</th>
<th>Deposition velocity (cm/s)</th>
<th>Molar yield (%)</th>
<th>6-MHO</th>
<th>Nonanal</th>
<th>Decanal</th>
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<tr>
<td>Tamas et al. [18]</td>
<td>0.19–0.27</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Weschler et al. [19]</td>
<td>–</td>
<td>2–3</td>
<td>2–5</td>
<td>1–4</td>
<td></td>
</tr>
<tr>
<td>Coleman et al. [20]</td>
<td>0.22–0.37</td>
<td>1–3</td>
<td>0.3–0.8</td>
<td>0.2–0.8</td>
<td></td>
</tr>
<tr>
<td>Rai et al. [21]</td>
<td>0.15–0.29</td>
<td>5–13</td>
<td>5–12</td>
<td>7–21</td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>0.15 ± 0.2</td>
<td>11.8 ± 0.5</td>
<td>2.0 ± 0.3</td>
<td>1.2 ± 0.3</td>
<td>3.0 ± 0.4</td>
</tr>
</tbody>
</table>

* Molar yields of selected VOCs were estimated and calculated based on figures and information from the references since they did not report the values directly.

* Data of the 3rd hour of reaction.
experiment since the molar yield of 6-MHO was much smaller than that of acetone. However, 4-OPA was not detected in our study. The main reason was that the HP-VOC column in our GC-MS was not able to separate dicarbonyls like 4-OPA from other compounds well. In future studies, we would try new methods to measure dicarbonyl products when secondary reaction was paid attention to.

3.4. Discussion about the EAR method

The EAR method has been proved to provide acceptable accuracy for investigating ozone reaction with skin-oiled clothing in Section 3.2. Moreover, it has several advantages compared with other methods: (i) It can obtain the profile of compounds from skin-oiled clothing and provide a better insight into the relationship between reactants and corresponding products in ozonation. (ii) The extracts from the skin-oiled clothing can be preserved for comparative experiments when quantity control of reactants is necessary. (iii) The method can be further extended to investigate ozone reaction with skin lipids on other surfaces, e.g. glass, wool and wood, by painting the extracts on target surfaces and then reacting with ozone in environmental chamber.

To further explore this topic, quantitative analysis of relationship between reactants and products may be needed. Therefore, quantification of compounds from skin-oiled clothing would be necessary in future study. Another possible improvement of the EAR method would be to obtain a more complete profile of compounds from skin-oiled clothing, such as wax esters and triglycerides.

4. Conclusions

This study aimed to investigate reactants and VOC products in the ozonation of skin-oiled clothing. An experimental method (EAR) was developed for investigation on VOCs formation in interactions between ozone and skin-oiled clothing. By implementing this experimental method, the following conclusions may be drawn:

The consistency in profile of extracts from skin-oiled clothing, and ozone deposition velocity on soiled clothing piece and molar yields of major VOC products in environmental chamber experiment, indicates that the EAR method can provide acceptable accuracy for investigation on ozone reaction with skin-oiled clothing. This method is particularly appropriate when information of reactants or quantity control of reactants is required in reaction analysis and experiment.

In the reaction between ozone and skin-oiled clothing, squalene and geranyl acetone are the major primary precursors for acetone and 6-MHO, of which acetone may also be formed by 2-methyl-2-docosene. The formation of nonanal would mainly attribute to unsaturated fatty acids, such as 9-octadecenoic acid and (Z)-7-hexadecenoic acid, and their derivatives like (Z)-13-docosenamide. 6-Hexadecenoic acid, the most abundant unsaturated fatty acid, and 8-Octadecenoic acid are the major contributors on generation of decanal. Wax esters and triglycerides with similar structure with these fatty acids also contribute to formation of nonanal and decanal.

<table>
<thead>
<tr>
<th>VOC Products</th>
<th>Possible primary precursors</th>
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</thead>
<tbody>
<tr>
<td>Name</td>
<td>Chemical structure</td>
</tr>
<tr>
<td>Acetone</td>
<td><img src="image1.png" alt="Chemical structure" /></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>6-MHO</td>
<td><img src="image4.png" alt="Chemical structure" /></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonanal</td>
<td><img src="image7.png" alt="Chemical structure" /></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Decanal</td>
<td><img src="image11.png" alt="Chemical structure" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The black dot• drawn on chemical structure represented the possible attacked double carbon-carbon bond in ozonation.
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References
