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Kinetics and Reaction Products of Ozone and Surface-Bound Squalene

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ABSTRACT: Because of the high occupant density in aircraft, the surface chemistry of ozone and squalene, an important component of skin oil, was evaluated. A reaction probability of $(45 \pm 14) \times 10^{-5}$ was determined for the reaction of squalene (2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene) with ozone (50 parts per billion (ppb)) on a glass plate surface using the Field and Laboratory Emission Cell (FLEC) Automation and Control System (FACS). To more clearly define part of squalene's indoor environment degradation mechanism, gas-phase and surface-bound products of the squalene+O_3 reaction were also investigated. Emitted products were captured in solution, derivatized with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA), and analyzed by gas chromatography and ion trap mass spectroscopy. The identified squalene+O_3 reaction products were: 6-methyl-5-hepten-2-one (6MHO, $((CH_3)_2C{=}CH(CH_2)_2\ C({=}O)CH_3)$), glyoxal (ethanedial, $HC({=}O)C({=}O)H$), 4-oxopentanal (4OPA, $CH_3C({=}O)CH_2CH_2\ CH({=}O)$), and 6,10-dimethylundeca-5,9-dien-2-one (geranyl acetone). The compound 5,9,13-trimethyltetradeca-4,8,12-trienal is proposed as the other major squalene+O_3 reaction product. This compound was determined from mass spectrometry coupled with plausible squalene+O_3 reaction mechanisms based on previously published volatile organic compound+O_3 gas-phase reaction mechanisms.

KEYWORDS: ozone, squalene, oxygenated organic compounds, kinetics, reaction products

Introduction

The aircraft cabin is a unique indoor environment that typically has a high occupant density and can experience ozone (O_3) concentrations in the 100 parts per billion (ppb) range [1–5]. Ambient ozone levels can be naturally elevated to hundreds of ppb at cruising altitudes, and this air is used to ventilate the aircraft cabin. Once ozone enters the cabin, it reacts predominantly with surfaces [4]. These reactions lower the cabin ozone concentration by an estimated 60 % to 80 % [2], but result in the production of oxygenated organic compounds such as aldehydes, ketones and dicarbonyls [1,2,4]. Recent research indicates that cabin surfaces such as seats, cabin interior plastics, and carpet react with ozone to form volatile organic compounds (VOCs) [2]. However, people are the dominant sink of ozone in the cabin environment [2–4]. Several studies have demonstrated that reactions with humans (even using clothing that has previously been exposed to skin oil as a surrogate for passengers) are responsible for 45 % to 60 % of the total ozone consumption in a fully loaded cabin [2,3,6]. A better understanding of the human+O_3 chemistry would benefit exposure assessment of the aircraft cabin environment and other occupied indoor environments where ozone is present, such as offices and homes.

Squalene (2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene) is a non-volatile alkene that constitutes ~5–15 % of skin oil or sebum [7]. Sebum is composed of fatty acids, cholesterol esters, and other unsaturated compounds. Squalene contributes nearly half of the carbon-carbon double bonds in sebum. The six carbon-carbon double bonds in squalene are likely to result in a rapid reaction with O_3 [8,9]. Volatile compounds that are the likely oxidation products of squalene have been detected in all of the recent studies of occupied cabin air quality [1–4,6]. As it is non-volatile, investigating squalene+O_3 surface chemistry would provide important insights to understand human impact on the indoor environment in aircraft.

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This paper reports the gas-phase emissions, surface-bound reaction products, and the surface reaction probability of the squalene+O_3 reaction. A recently developed system for conducting surface chemistry experiments coupled with analytical techniques to detect oxygenated organic compounds was used to investigate this important reaction [10].

Experimental

Apparatus

Experiments to measure the reaction product emissions and reaction probability of the squalene+O_3 system were conducted with a previously described Field and Laboratory Emission Cell (FLEC) Automation and Control System (FACS) [10]. A brief description is provided here. For these experiments, the FLEC surfaces were treated with an inert silicon coating via a commercial process (Restek, Bellefonte, PA). Ozone, humidity, and flow rate are monitored and controlled using an ultraviolet ozone monitor (Thermo Electron 49i, Waltham, MA) and humidity (Honeywell HIH-3602-L-CP, Freeport, IL) and flow sensors (Aallborg, Orangeburg, NY). The output flow was connected to the FLEC input, which was placed on the prepared glass plate (described below). Thus, specific ozone concentrations (50 ppb and 100 ppb) and flow rates (300 $\mathrm{ml \cdot min^{-1}}$ and 750 $\mathrm{ml \cdot min^{-1}}$) could be delivered to the glass plate/chemical of interest. The output of the FLEC was either collected in an impinger to trap gas-phase reaction products or mixed with zero air and fed to an external ultraviolet ozone monitor to determine output ozone concentration.

Squalene+ozone reaction products were determined by coating a plate with a 1 % (8.3×10^{14} $\mathrm{molecules \cdot cm^{-2}}$) solution of squalene in methanol using the spraying technique described below. The FACS conditions were 300 $\mathrm{ml \cdot min^{-1}}$, 100 ppb O_3, and 50 % relative humidity (RH). The reaction product emissions were collected for approximately 4 h in 14.7 mL methanol in an impinger (Kontes, Vineland, NJ) submerged in an ice bath to minimize evaporative losses.

Reaction product identification experiments were performed utilizing direct sampling and chemical derivatization methods. The gas-phase aldehyde and ketone reaction products were derivatized to organic oximes using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) [11]. For the impinger sample, 200 μL of 20 mM PFBHA solution was added to 2 mL of impinger solution. The rest of the sample (approximately 8 mL) was sealed in a vial for further analysis. The reacted glass plate was rinsed twice with 3-mL aliquots of methanol. The rinsate was collected in a clean glass container, and 2 mL were removed and combined with 200 μL of 20 mM PFBHA solution. Derivatized reaction products were analyzed with a Varian (Palo Alto, CA) 3800 gas chromatograph (GC) and a Varian Saturn 2000 ion trap mass spectrometer (MS) operated in the electron impact (EI) mode. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32 mm I.D., 30 m long, 1 μm film thickness) column and the following GC oven parameters: 60°C for 1 min, then10°C$\cdot \mathrm{min^{-1}}$ to 280°C and held for 10 min. Samples were injected in the splitless mode, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 60°C for 1 min, then 180°C$\cdot \mathrm{min^{-1}}$ to 250°C and held to the end of the chromatographic run. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full scan EI ionization spectra were collected from m/z 40 to 650. Chemical ionization (CI) mass spectra using acetonitrile were also collected on the derivatized reaction products allowing the determination of the PFBHA-derivatized compound's molecular weight.

For determining squalene+O_3 reaction probability, separate chemical stock solutions of squalene (4.2×10^{-5} M), tricosene (4.2×10^{-5} M), or oleic acid (5.0×10^{-5} M) were prepared in methanol. Oleic acid was evaluated to validate the measured reaction probability against literature values. Tricosene was chosen as a species similar to squalene, but containing one double bond. These stock solutions were used straight or diluted in methanol to achieve lower surface coverage. Squalene, oleic acid, and tricosene are very low vapor pressure oils and are not expected to evaporate from the glass plate after application. One mL of the prepared solution of interest was sprayed onto a glass plate (McMaster Carr, Aurora, OH) utilizing a modified artist's air brush (Badger Franklin Park, IL, part number 350 with fine tip) to generate a fine mist. Sample area was controlled by the use of an aluminum template (6.5 in. (16.5 cm) diameter) to ensure the coated section of the glass plate was smaller than the area of the FLEC's sealing o-ring (7.44 in (18.9 cm) diameter). The plate was sprayed with the solution of interest and the methanol solvent was allowed to evaporate for approximately 5 min. Note that applying 1 mL of stock solution over the 214 $\mathrm{cm^2}$

spray area resulted in roughly monolayer coverage of the glass with the compound of interest. Plates coated with 1 mL of methanol only, followed by 5 min evaporation time, simply demonstrated a step decrease (~8 %) of ozone concentration that remained stable until the FLEC/glass plate was removed from the system, indicating just ozone/glass reaction. The FACS was set to deliver either 50 ppb or 100 ppb ozone at 50 % relative humidity and 750 mL·min^{-1}.

For experiments where reaction kinetics were determined (versus experiments designed to determine gas-phase products where the exhaust was bubbled through an impinger), the O_3 level was measured at the exhaust of the FLEC using a Thermo 49i photometric O_3 monitor (ThermoScientific, Franklin, MA). Zero air was used as a make-up air to provide a high enough flow rate for the O_3 monitor. The output of the O_3 monitor was collected every 30 s using a computer and in-house developed software. O_3 was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon® bag.

Reagents

All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): squalene (98 %), *cis*-9-tricosene (97 %), *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) (98+ %), 6-methyl-5-hepten-2-one (99 %); from Fisher Scientific (Pittsburgh, PA): oleic acid (lot number 064052, >97 %), methanol (HPLC grade 99.9 %); from Richman Chemical (Lower Gwynedd, PA): 4-oxopentanal (98.84 %). Water was distilled, deionized to a resistivity of 18 MΩ·cm, and filtered using a Milli-Q® filter system (Billerica, MA). Zero Air, the diluent gas, was supplied by Amerigas (Sabraton, WV) and used as received.

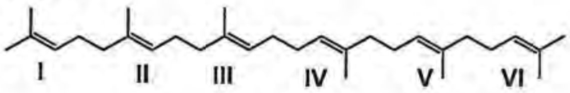
Experiments were carried out at (297 ± 3) K and 1 atmosphere pressure.

Results

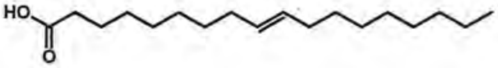
Squalene's labeled reactive molecular structure is shown in Structure 1.

Structures

Squalene
Structure 1



Oleic Acid
Structure 2



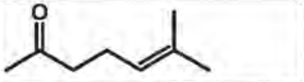
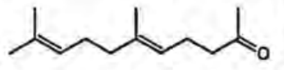
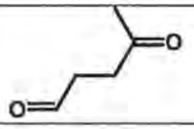
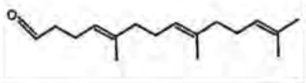
Tricosene
Structure 3

The presence of six carbon-carbon double bonds, each with a branching methyl group, in the molecular chain results in a calculated ozone rate constant of 2.6×10^{-15} cm^{3}·molecule^{-1}·s^{-1} using EPA's AOPWIN structure reactivity-based rate constant calculator [12]. This is approximately one order of magnitude greater than that for a highly reactive terpene such as limonene [8]. The use of squalene/ozone/glass plate system to simulate squalene+ozone chemistry on skin has been documented before [7].

Squalene+O_3 Reaction Products

The reaction products observed from the squalene+O_3 addition to the carbon-carbon double bond are listed in Table 1. The squalene+O_3 reaction products observed and positively identified using the pure compound for verification by derivatization were: ethanedial (glyoxal, $HC(=O)C(=O)H$), 6-methyl-5-hepten-2-one ($(CH_3)_2C=CH(CH_2)_2C(=O)CH_3$), 4-oxopentanal ($CH_3C(=O)CH_2CH_2C(=O)H$) and 6,10-dimethylundeca-5,9-dien-2-one (geranyl acetone). Structures and ions used to identify these

TABLE 1—*Molecular structure of some squalene+O_3 reaction products.*

Retention time (min)	Name	Molecular Weight (amu)	Structure	CI ions observed
14.4, 14.9	6-methyl-5-hepten-2-one	126		322
24.1, 24.5	Ethanedial (glyoxal)	58		449
26.8, 27.5	6,10–dimethylundeca-5,9 –dien-2-one (geranyl acetone)	194		390
30.0, 30.3, 30.7	4-Oxopentanal	100		491
38.4, 39.1	5,9,13 –trimethyltetradeca-4,8,12-trienal	248		444

compounds are listed in Table 1. Elucidation of the other major reaction product (5,9,13-trimethyltetradeca-4,8,12-trienal) was facilitated by mass spectrometry of the derivatized reaction product coupled with plausible squalene+O_3 reaction mechanisms based on previously published volatile organic compound+O_3 gas-phase reactions as described below [8,13].

Derivatization of nonsymmetric carbonyls using PFBHA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes (Fig. 1). Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical. Typically, the mass spectra of the PFBHA-derivatized oximes (generic structure: $F_5C_6CH_2ON{=}C(R_1)(R_2)$) include an ion at m/z 181 ($[CH_2C_6F_5]^+$ fragment) with a large relative intensity (>40 %) and a [PFBHA oxime+181]$^+$ ion (due to reactions in the ion trap mass spectrometer) [11]. In most cases, the m/z 181 ion relative intensity for the chromatographic peaks of squalene+O_3 reaction product oximes was either the largest or one of the largest in the mass spectrum and was used to generate selected ion chromatograms. The product data are described below.

The following chronological chromatographic retention time results and mass spectra data were observed utilizing PFBHA derivatization and the Varian 3800/Saturn 2000 GC/MS system. The chromatographic peaks for reaction products were observed only after addition of O_3 to squalene/methanol/air. Derivatization experiments performed using squalene only dissolved in methanol, did not result in any of the data reported below except for small amounts (as noted by chromatographic peak areas) of ethanedial (glyoxal). However, the glyoxal peak areas increased significantly, between 180 % to 380 %, with

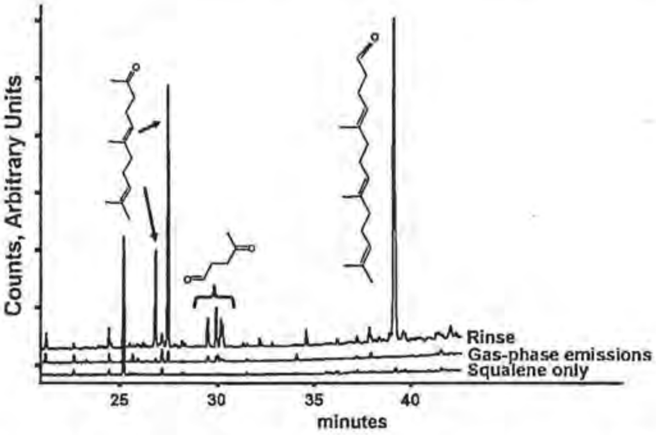


FIG. 1—*Gas chromatogram of PFBHA derivatized samples from squalene+O_3 on a glass plate experiments. Chromatograms are offset for clarity. All peaks are on the same scale. Molecular structures label the chromatographic peaks discussed in the text.*

squalene+O_3 reaction initiation, indicating that glyoxal is a likely product of the squalene+O_3 reaction. Given that the squalene molecule contains six double bonds it is not surprising that some oxidation can occur. The formation of oxidation products has been observed previously in limonene and other terpene VOCs during routine long term storage [14–17]. Acetone has been previously observed as a significant squalene+O_3 reaction product and would be expected to be observed in the experimental system described here unless it was volatilized in the impinger and swept out of the system during sampling [1,2,4,9]. However, the PFBHA and acetone-oxime peaks were not chromatographically resolved using the parameters described above. To date no acetone yields have been reported.

6-Methyl-5-hepten-2-one (6MHO, $((CH_3)_2C{=}CH(CH_2)_2C({=}O)CH_3)$)

The chromatographic peak for the oxime observed at 14.4 min and 14.9 min was observed as a reaction product of squalene+O_3 rinse experiments and had ions at m/z (relative intensity) 181 (100 %) and 82 (33 %). Using acetonitrile for chemical ionization (CI), and M+1 ion of m/z of 322 was observed for the PFBHA-derivatized sample yielding a molecular mass of 126. The PFBHA-6MHO oxime was synthesized to confirm this chromatographic assignment [11]. This carbonyl compound was observed in both the gas-phase and rinse experiments.

Ethanedial (Glyoxal, $HC({=}O)C({=}O)H$)

The chromatographic peaks for the oxime observed at 24.1 min and 24.5 min were observed as a reaction product of squalene+O_3 and had ions at m/z (relative intensity) 181 (100 %) and 448 (25 %). The m/z 448 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 58. Using acetonitrile for chemical ionization, an M+1 ion of m/z of 449 was observed for the PFBHA-derivatized sample. The PFBHA-glyoxal oxime was synthesized to confirm this chromatographic assignment [11]. This carbonyl compound was observed in both the gas-phase and rinse experiments.

6,10-Dimethylundeca-5,9-dien-2-one (Geranyl Acetone)

The chromatographic peaks for the oxime observed at 26.8 min and 27.5 min were observed as a reaction product of squalene+O_3 in both gas-phase emissions and glass plate rinse samples and had ions at m/z (relative intensity): 41 (25–60 %), 181 (30–90 %), 69 (100 %), 181 (90 %) 208 (35 %), 320 (100 %), and 346 (15 %). Using acetonitrile for chemical ionization, an ion of m/z of 458 (<5 %) along with a m/z of 390 (100 %) was observed for the PFBHA-derivatized sample. The [M+1] m/z 390 ion could be the result of a single PFBHA derivatization indicating a reaction product with a molecular weight of 194. The addition of 68 mass units to yield the m/z 458 could be the result adding the $((CH_3)_2C{=}CHCH_2)$ moiety via an ion trap reaction [11]. Based on the molecular weight, probable squalene+O_3 reaction mechanisms, and mass spectra data, a molecular structure of 6,10-dimethylundeca-5,9-dien-2-one (geranyl acetone) is assigned to this chromatographic peak [1]. The PFBHA-geranyl acetone oxime was synthesized to confirm this chromatographic assignment [11]. This carbonyl compound was observed in both gas-phase and rinse experiments.

4-Oxopentanal (4OPA, $CH_3C({=}O)CH_2CH_2CH({=}O)$)

The oxime observed with a chromatographic peak at a retention time of 30.0, 30.3, and 30.7 min had ions of m/z (relative intensity) 82 (16–23 %), 181 (65–100 %), 262 (15–20 %), 263 (17–22 %), 278 (34–51 %), 279 (76–100 %), and 490 (11–17 %), as seen in Fig. 1. The m/z 490 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 100. Using acetonitrile for chemical ionization, an M+1 ion of m/z of 491 was observed for the PFBHA-derivatized sample. The PFBHA-4OPA oxime was synthesized to confirm this chromatographic assignment [11]. This dicarbonyl was observed in both gas-phase and rinse experiments [1,3].

Oxime at Retention Times 38.4 min and 39.1 min

The chromatographic peaks for the oxime observed at 38.4 min and 39.1 min were observed as a reaction product of squalene+O_3 only in the glass plate rinse experiments and had ions at m/z (relative intensity):

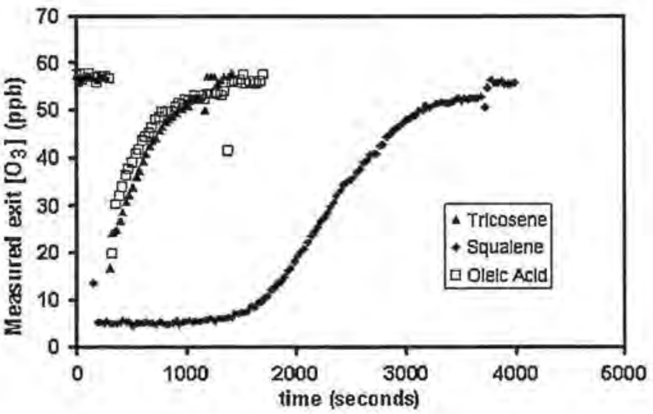


FIG. 2—*Plot of* $[O_3]$ *leaving the FLEC/coated glass plate system as a function of time. Surface coverages are: Squalene (♦)* 1.2×10^{14} *molecules*$\cdot$*cm*$^{-2}$*, tricosene (▲)* 1.2×10^{14} *molecules*$\cdot$*cm*$^{-2}$*, and oleic acid (□)* 1.4×10^{14} *molecules*$\cdot$*cm*$^{-2}$*.*

41 (60 %), 69 (100 %), 81 (70 %), 95 (40 %), 181 (50 %), 246 (75 %), and 262 (40 %). Using acetonitrile for chemical ionization, an ion of m/z of 512 (15 %) along with a m/z of 444 (100 %) was observed for the PFBHA-derivatized sample. Assuming the $[M+1]$ is the m/z 444 ion, a single PFBHA-derivatized reaction product with a molecular weight of 248 is determined. The observed m/z 512 is an addition of 68 mass units to the m/z 444, and could be the result of adding the $((CH_3)_2C{=}CHCH_2)$ moiety via an ion trap reaction [11]. Based on the molecular weight, probable squalene+O_3 reaction mechanisms, and mass spectra data, a structure of 5,9,13-trimethyltetradeca-4,8,12-trienal is assigned to this chromatographic peak.

Reaction Probabilities Determined Using the FACS

From the reaction product results presented above, it is obvious that squalene and squalene reaction products are reacting with ozone on the surface. As can be seen clearly in Fig. 2, a squalene surface coverage of 1.2×10^{14} molecules$\cdot$cm^{-2}, which corresponds to roughly monolayer coverage, was able to completely consume, at the transport limited rate, 100 ppb of ozone for 22 min before enough of the squalene and its reaction products are sufficiently depleted to allow the outlet O_3 concentration to increase. While reaction rates among double bonds in polyalkenes may differ substantially [18,19], Moise and Rudich show that the two unsaturations in linoleic acid exhibit similar reaction rates [20]. Due to the repetitive structure of squalene, its unsaturations may also exhibit similar rates. Because we are unable to distinguish reaction sites, an average reactivity for each carbon-carbon double bond was used for the purposes of determining a reaction probability. This assumption simplifies the mathematical interpretation of the data while providing an assessment of the overall O_3+squalene reaction probability rather than that for a specific site.

Interpretation of Kinetics

The FLEC device can be used to derive surface kinetic information when operated under favorable conditions. Ozone contact surface reactants, and ozone conversion rates are determined by measuring the inlet and outlet ozone concentrations. As the surface species is consumed, the ozone conversion rate decreases. The system is inherently second order, in that the concentration of both ozone and surface reactants are changing simultaneously. However, evaluating the system over a modest time interval, or a modest change in ozone concentration, pseudo-first-order kinetics can be assumed. Further, by evaluating only that region where surface kinetics limit ozone uptake, we can neglect the fact that transport conditions within the FLEC are non-uniform [21].

Pseudo-First-Order Analysis

The second-order rate equation for the reaction of ozone with a surface reactant, where S is the surface concentration, is

$$\text{rate} = \frac{dS}{dt} = -k_2 C_{\text{film}} S \tag{1}$$

where k_2 is the second-order rate coefficient ($\text{ppb}^{-1}\cdot\text{s}^{-1}$) and C_{film} is the gas-phase ozone concentration adjacent to the squalene coated surface. Because we assess the kinetics in the region where uptake is limited by surface reaction rates (not transport through a boundary layer), the film concentration C_{film} is nearly equal to $C_{\text{ozone\_outlet}}$. Note that the pseudo-first-order rate coefficient k_1 is therefore equal to $k_2 C_{\text{ozone\_outlet}}$. By a mass balance on ozone within the FLEC, and assuming no ozone loss on the FLEC surfaces,

$$\text{rate} = -Q(C_{\text{ozone\_inlet}} - C_{\text{ozone\_outlet}}) \tag{2}$$

The term Q is the flow rate. For a short time interval, $C_{\text{ozone\_outlet}}$ is approximately constant, so Eq 1 can be solved:

$$\ln(S) - \ln(S_o) = -k_2 C_{\text{ozone\_outlet}} t \tag{3}$$

This is an approximate solution for a short time interval over which $C_{\text{ozone\_outlet}}$ changes a small amount. A plot of $\ln(S)$ versus t will yield a slope of $-k_2 C_{\text{ozone\_outlet}}$. In this system, we are unable to measure S directly. However, the ozone conversion rate is an indirect measure of the change in S, and by combining Eqs 1 and 2, the following emerges:

$$k_2 C_{\text{ozone\_outlet}} S = Q(C_{\text{ozone\_inlet}} - C_{\text{ozone\_outlet}}) \tag{4}$$

Rearrange and take logarithm:

$$\ln(S) = \ln\left(\frac{Q}{k_2}\right) + \ln\left[\frac{C_{\text{ozone\_inlet}} - C_{\text{ozone\_outlet}}}{C_{\text{ozone\_outlet}}}\right] \tag{5}$$

Combining Eqs 5 and 3:

$$\ln\left(\frac{Q}{k_2 S_o}\right) + \ln\left[\frac{(C_{\text{ozone\_inlet}} - C_{\text{ozone\_outlet}})}{C_{\text{ozone\_outlet}}}\right] = -k_2 C_{\text{ozone\_outlet}} t \tag{6}$$

The slope, i.e., $-k_2 C_{\text{ozone\_outlet}}$, or k_1, is derived by plotting:

$$\ln\left[\frac{(C_{\text{ozone\_inlet}} - C_{\text{ozone\_outlet}})}{C_{\text{ozone\_outlet}}}\right] \text{ versus } t. \tag{7}$$

The reaction probability is then derived from k_2, the gas density, ρ (10^9 ppb), and the ozone-reactant collision rate, Z ($3.5 \times 10^9\ \text{s}^{-1}$):

$$\gamma = \frac{k_2 \rho}{Z} \tag{8}$$

The ozone-reactant collision rate Z was estimated from the wall collision rate for ozone at 297 K ($2.26 \times 10^{23}\ \text{cm}^{-2}\cdot\text{s}^{-1}$) and the cross-sectional area of a squalene molecule ($1.5 \times 10^{-14}\ \text{cm}^{-2}$), estimated from its molecular volume and assuming cylindrical geometry [22,23].

Data Analysis

The foregoing analysis is based on the assumption that the conversion rates are equal at all locations within the reactor and that the reactor is well mixed. Because the FLEC approximates a radial plug-flow reactor, it is necessary to consider only that data derived from near the end of an experiment, where the inlet (outer radius) and outlet (center point) concentrations are similar. We only analyze data where the ratio of the outlet to inlet ozone mixing ratios (C/C_o) is between 0.70 and 0.94. In this range, uncertainty due to inhomogeneous ozone concentrations is less than 20 % [24]. The lower limit also corresponds to a point where the surface kinetic resistance to ozone uptake is about six times the mass-transfer resistance, ensuring that kinetics overwhelm transport effects. The upper limit is based on uncertainty associated with measuring small ozone differences when C approaches C_o.

To validate the kinetic analysis method, the reaction probability of oleic acid was evaluated and compared against the reaction probabilities of frozen and liquid oleic acid (a component of atmospheric

TABLE 2—*Chemical reaction probabilities determined from experiments.*

Chemical	Surface coverage, molecules/cm^{-2}	Inlet [O_3], ppb	Reaction rate constant, $\times 10^{16}$ molecule·s·cm^{-3}[a]	Reaction probability, $\gamma \times 10^{4}$[b]
Squalene			26	
	1.2×10^{13}	50		4.5 ± 1.4
	1.2×10^{13}	100		3
Tricosene			1.3	
	3.5×10^{13}	50		0.6
	1.2×10^{14}	50		0.65
	1.2×10^{14}	100		0.5
Oleic Acid			1.3	
	1.4×10^{14}	100		0.5
	Liquid			8.3 ± 0.2[c]
	Frozen			0.52 ± 0.01[c]

[a] Calculated using AOPWin [12].

[b] Determined from data.

[c] from Ref. [20].

organic aerosols) that have been recently determined [20]. Oleic acid (Structure 2) is different from squalene in two significant ways: the carboxylic acid end and the lone unbranched carbon-carbon double bond in the molecular chain. Oleic acid was deposited on a glass plate at an estimated 1.4×10^{14} molecules·cm^{-2}. The inlet O_3 was controlled at 100 ppb and injected at 750 mL·min^{-1}. As can be seen in Fig. 2, the outlet ozone concentration profile is very different from the one observed for squalene at a similar surface coverage and experimental parameters. Using the kinetic analysis described above a reaction probability γ of 5×10^{-5} was observed. This value is in agreement with the reaction probability $(5.2 \pm 0.1) \times 10^{-5}$ measured by Moise and Rudich for frozen oleic acid (Table 2) [20].

Similar to oleic acid, *cis*-9-tricosene (tricosene), Structure 3, is a large organic molecule with a single unbranched carbon-carbon double bond in the middle of the molecular chain. However, tricosene does not have a carboxylic acid group on the end of the molecule and is more representative of the squalene molecule. To determine the reaction probability, experiments were conducted with a surface coverage range of 0.35×10^{14} to 1.2×10^{14} molecules·cm^{-2}, 50 % RH, 750 mL·min^{-1}, and 50 ppb or 100 ppb ozone. Using the kinetic analysis described above a reaction probability γ between 5×10^{-5} and 6.5×10^{-5} was observed. (Table 2) From Fig. 2 it can be clearly seen that both oleic acid and tricosene have very similar O_3 concentration versus time profiles indicating a similar oxidation rate by O_3 addition to the carbon-carbon double bond.

Squalene Analysis

It is assumed, in Eqs 1 and 2, that each surface reactant is converted to a non-reactive species. In the case of squalene, with six carbon-carbon double bonds, the first generation reaction products can be low-volatility (remain on the surface) oxygenated organic compounds with multiple carbon-carbon bonds that can also react readily with available ozone. To approximate the reaction probability for this compound, we assume that squalene is composed of six subunits, each with molecular weight 68.3 g·mol^{-1} and each assumed to have the same reactivity. The reaction probability corresponds to the subunit, but also to the probability that ozone will react with squalene if it strikes anywhere along the molecule.

In these experiments, ozone reaction kinetics are determined from the rate of increase in the ozone outlet concentration. Clearly, from Fig. 2, a surface coverage of 1.2×10^{14} molecules·cm^{-2} is too concentrated to accurately determine squalene's ozone reaction probability; by the time the ozone concentration at the exhaust starts increasing it is likely that most of the squalene has been consumed and most ozone reactions are with oxidation products. Reducing the surface coverage by an order of magnitude to 1.2×10^{13} molecules·cm^{-2} was expected to better capture the reaction of ozone with squalene. As can be seen in the Fig. 3 inset plot, using this lower surface coverage eliminated the complete ozone consumption phase seen in Fig. 2. Applying the kinetic analysis above and plotting Eq 7 above resulted in the linear plot in Fig. 3. Multiple experiments at 1.2×10^{13} molecules·cm^{-2} surface coverage, 50 % RH, 750 mL·min^{-1}, and 50 ppb and 100 ppb ozone were used to determine squalene's reaction probability with ozone on a surface. Reaction probabilities of $\sim 30 \times 10^{-5}$ and $45 \pm 14 \times 10^{-5}$,were determined for 100 ppb and 50 ppb

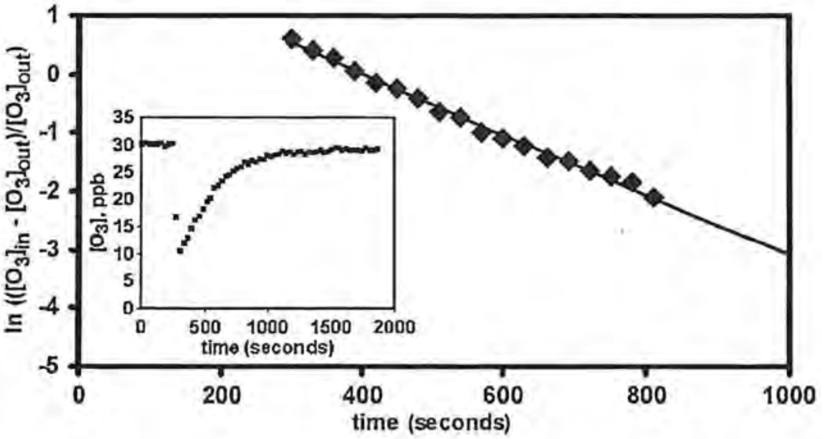


FIG. 3—*Kinetic analysis, described in the text, of squalene* (1.2×10^{13} *molecule*$\cdot$*cm*$^{-2}$)$+O_3$ *on a glass plate. Inset plot is same experiment, but* $[O_3]$ *vs time.*

ozone, respectively. The stated error is the standard deviation of the data set. Formation of oxidized products, and evaporation of more volatile products (e.g., 6-MHO), can alter surface reactivity as the reaction proceeds. Therefore, reaction probability estimates from early in the experiment better reflect ozone-squalene kinetics.

Discussion

O_3 reacts with squalene by addition to the carbon-carbon double bonds [8]. The "reactive structure" of squalene can be drawn as shown in Structure 1. The possible mechanistic steps leading to product formation are described below and shown in Fig. 4.

6-Methyl-5-hepten-2-one (6MHO, $((CH_3)_2C{=}CH(CH_2)_2C({=}O)CH_3)$*)*

6MHO has been observed before as an ozone reaction product from squalene [1,4,9]. 6MHO formation could be the result of two main reaction pathways: 1) ozone addition to carbon-carbon double bond II or V (Structure 1), forming the respective ozonide and dissociating to 6MHO and $O{=}C(CH_2)_2C(CH_3){=}CH({-}(CH_2)_2CH{=}C(CH_3){-})_3$ and 2) as a secondary reaction product of geranyl acetone or 5,9,13-trimethyltetradeca-4,8,12-trienal (Fig. 4). However, if pathway 1 occurred, the product $O{=}C(CH_2)_2C(CH_3){=}CH({-}(CH_2)_2CH{=}C(CH_3){-})_3$ would be expected to adhere to the glass plate and would possibly be observed in the rinse/PFBHA experiments as an oxime with a molecular ion m/z of 527. This was not observed in the experimental system as described, which could be because all of the $O{=}C(CH_2)_2C(CH_3){=}CH({-}(CH_2)_2CH{=}C(CH_3){-})_3$ further reacted or because it did not dissolve in methanol and thus could not be rinsed from the glass plate.

Ethanedial (Glyoxal, $HC({=}O)C({=}O)H$*)*

Because glyoxal is a dicarbonyl, it is almost certainly a third or fourth generation reaction product [8]. The mechanism leading to its formation is not straightforward. It could be a surface-enhanced reaction product.

6,10-Dimethylundeca-5,9-dien-2-one (Geranyl Acetone)

This ketone is likely formed as a primary product from ozone addition to the III or IV carbon-carbon double bond (Structure 1) of the squalene molecule (Fig. 4). Geranyl acetone has been observed in the gas-phase emissions of recent simulated occupied aircraft experiments [1]. As can be seen from the chromatogram in Fig. 1, geranyl acetone also adheres to the glass plate and was observed in the rinse data, indicating that once formed it could be available for additional surface reactions with ozone.

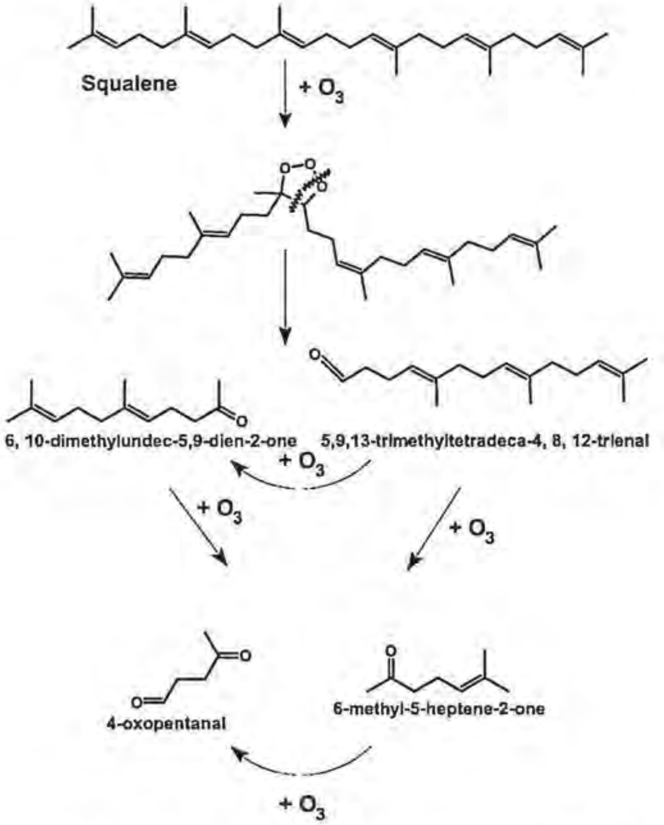


FIG. 4—*Reaction mechanism for squalene* $+O_3$ *showing the formation of 6, 10-dimethylundec-5,9-dien-2-one (geranyl acetone), 5,9,13-trimethyltetradeca-4,8,12-trienal, 4-oxopentanal (4OPA), and 6-methyl-5-heptene-2-one (6MHO).*

4-Oxopentanal (4OPA, $CH_3C(=O)CH_2CH_2CH(=O)$*)*

Similar to glyoxal above, 4OPA is not likely a primary squalene+ozone reaction product. This dicarbonyl compound is likely a primary ozonolysis product of 6MHO, or a secondary ozonolysis reaction product of squalene via 6,10-dimethylundeca-5,9-dien-2-one and/or 5,9,13-trimethyltetradeca-4,8,12-trienal [13].

Oxime at Retention Times 38.4 min *and* 39.1 min *(Proposed to be 5,9,13-trimethyltetradeca-4,8,12-trienal):*

The mechanism for 5,9,13-trimethyltetradeca-4,8,12-trienal formation is shown in Fig. 4. This product was found only in the glass plate rinse experiments (Fig. 1) indicating that once formed it could be available for additional reaction with ozone on the surface. It is unusual that glyoxal and 4OPA are the only dicarbonyl compounds observed from the squalene+O_3 system. Since there was a constant supply of O_3 in the system it is not unreasonable to expect the diene and triene reaction products would react with ozone further forming more oxygenated organic products.

Based on the data presented in Table 2, for every million ozone molecule encounters with a squalene molecule on the surface, approximately 400 will lead to reaction. An additional comparison can be made between the calculated gas-phase reaction rate constant and the surface reaction probability. Multiplying the calculated second-order squalene-ozone rate constant (2.6×10^{-15} $cm^3\cdot molecule^{-1}\cdot s^{-1}$) by the gas density ($2.5\times10^{19}$ $molecules\cdot cm^{-3}$ at 298 K) and dividing by the bimolecular collision rate (3×10^9 s^{-1}) yields a gas-phase reaction probability of 2.2×10^{-5} [12]. Comparing the surface reaction probability from the data in Table 2, a 20-fold enhancement in the squalene+O_3 reaction is realized.

Summary

In the aircraft environment, the squalene present on human occupants' skin and clothing can react with the ozone to form several oxygenated organic compounds. Ozone reactions with squalene on a glass plate were investigated, and reaction products were determine using PFBHA-derivatization. The products measured in the gas phase and on the surface include the carbonyls 6MHO and geranyl acetone and the dicarbonyls 4OPA and glyoxal. The formation of dicarbonyl compounds may play a role in occupant health effects [25]. Geranyl acetone, 6MHO and 4OPA have been observed in simulated aircraft cabin environments. The work presented here also revealed that a long chained triene aldehyde adhered to the surface and would be available for additional surface reaction with ozone. The reaction probability ($45 \pm 14 \times 10^{-5}$) observed for squalene is among the highest measured for ozone reacting with a surface species and is consistent with reaction probabilities for soiled clothing [2] and hair [26].

Additional improvements in near real time ozone monitoring and sampling volume would allow these experiments to be conducted at lower inlet O_3 concentrations. Further kinetic and product yield analyses of pure and mixed components of human skin oil will be necessary to estimate the proportional product formation rate from each unsaturated component of skin oil.

Acknowledgments

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