

# Gas chromatography of trimethylsilyl derivatives of $\alpha$ -methoxyalkyl hydroperoxides formed in alkene–O<sub>3</sub> reactions

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## Abstract

The synthesis of trimethylsilyl (TMS) hydroperoxide derivatives for gas chromatography (GC) was studied using *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) for derivatization of cumene hydroperoxide (CMOOH) ( $\alpha,\alpha'$ -dimethylbenzyl hydroperoxide) and  $\alpha$ -methoxyalkyl hydroperoxides formed by liquid- and gas-phase ozonolysis of a series of terminal alkenes in the presence of methanol (CH<sub>3</sub>OH). Derivatization efficiencies >90% were achieved over a wide range of solution concentrations. The major compounds identified by GC–mass spectrometry of the derivatized products of alkene–O<sub>3</sub> reactions were  $\alpha$ -methoxyalkyl hydroperoxides, methyl esters, and aldehydes. Yields of  $\alpha$ -methoxyalkyl hydroperoxides and methyl esters were quantified using effective carbon numbers (ECNs) and used to determine the yields of stabilized Criegee intermediates (SCIs) from gas-phase ozonolysis reactions. Such measurements are important for understanding the atmospheric chemistry of alkene emissions. SCI yields measured for the reactions of 1-octene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH=CH<sub>2</sub>], 1-nonene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CH=CH<sub>2</sub>], and 2-methyl-1-octene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>C(CH<sub>3</sub>)=CH<sub>2</sub>] are consistent with previous measurements or predictions based on literature data. SCI yields measured for the reactions of 1-decene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH<sub>2</sub>], 1-dodecene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>CH=CH<sub>2</sub>], and 1-tetradecene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>CH=CH<sub>2</sub>] are much lower than expected, apparently due to side reactions with low volatility aldehydes that form peroxyhemiacetals, which are not amenable to GC analysis. In general, the results indicate that off-line MSTFA derivatization can be an efficient means for increasing the stability of thermally labile hydroperoxides for identification and quantitation by GC, and offers a new approach for the analysis of these environmentally important compounds.

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## 1. Introduction

The oxidation of alkenes by O<sub>3</sub> is an important atmospheric photochemical process, particularly in polluted urban areas where O<sub>3</sub> concentrations are often much greater than in remote locations [1]. Although the kinetics, products, and mechanisms of gas-phase alkene ozonolysis reactions have been extensively studied (see reviews by Atkinson [2] and Calvert et al. [3]), there remain significant uncertainties, as demonstrated by the general lack of mass balance between reacted alkenes and identified products.

The reaction of O<sub>3</sub> with alkenes begins with the addition of O<sub>3</sub> across the carbon–carbon double bond to form an energy-rich primary ozonide. The ozonide rapidly decomposes to form, in the case of the terminal alkenes studied here, two pairs of products: a large excited Criegee intermediate ([R<sub>1</sub>CHOO]<sup>‡</sup>) and formaldehyde (HCHO) by reaction (R1a), and a C<sub>1</sub> excited Criegee intermediate ([CH<sub>2</sub>OO]<sup>‡</sup>) and a large aldehyde (R<sub>1</sub>CHO) by reaction (R1b), where R<sub>1</sub> is an alkyl group.

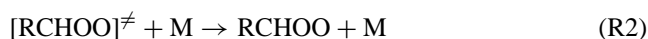


The yield of each of the primary carbonyls formed from ozonolysis of unsubstituted C<sub>3</sub>–C<sub>10</sub> terminal alkenes is 0.5

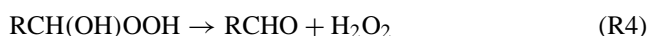
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(within experimental uncertainties). The fates of Criegee intermediates (CIs) are not completely understood, however, even for reactions of small alkenes. Excited CIs can isomerize, decompose, or be stabilized by collisions with air molecules, and the stabilized Criegee intermediates (SCIs) can subsequently undergo unimolecular or bimolecular reactions. In the latter case, SCIs can be converted to a carbonyl by reaction with CO, NO, or SO<sub>2</sub> (by O-atom abstraction), they can react with carbonyls to form secondary ozonides, or they can react with water, alcohols, or carboxylic acids to form  $\alpha$ -substituted hydroperoxides. Pathways leading to the latter compounds are of particular importance to the present study and are shown in reactions (R2) and (R3), where R = R<sub>1</sub> or H, G = H, or an alkyl or acyl group, and M is a third body (N<sub>2</sub> or O<sub>2</sub> for reaction in air).



An important quantity for evaluating the potential contributions of various reaction pathways in the above mechanism is the fraction of reacted alkene that is collisionally stabilized. SCI yields have generally been estimated by measuring product yields for reactions conducted in the presence of an SCI scavenger. These measurements can be difficult, however, because many of the products of SCI-scavenger reactions are difficult to analyze with conventional techniques. One approach has been to measure the sulfuric acid aerosol formed from the SO<sub>3</sub> product of the reaction of SO<sub>2</sub> with SCIs under humid conditions [4]. More recently, SCI yields have been determined by measuring  $\alpha$ -hydroxyhydroperoxides formed by reaction (R3) in the presence of water, and H<sub>2</sub>O<sub>2</sub> and aldehydes formed by decomposition of the hydroxyhydroperoxides (R4) [5,6].



Organic hydroperoxides and H<sub>2</sub>O<sub>2</sub> were measured using high performance liquid chromatography with fluorescence detection, while aldehydes were characterized by GC-flame ionization detection (FID). Because H<sub>2</sub>O<sub>2</sub> and the aldehydes have sources in addition to reaction R4, the SCI yields were calculated from measurements made for reactions conducted with and without water as an SCI scavenger.

One disadvantage of the approaches described above is that they measure the total SCI yield rather the individual yields of the large and small SCIs. Greater detail is necessary for developing a more complete mechanism for these reactions. This can be especially important, for instance, in understanding pathways that lead to aerosol formation, since it is generally only large SCIs whose reaction products can have sufficiently low volatility to condense into particles. Furthermore, it would be preferable to use a method for quantifying SCI yields that relies on the measurement of compounds (preferably a single compound) whose only source is the SCI-scavenger reac-

tion, rather than having to deal with the uncertainty that is inherent in a measurement that involves the quantification of a number of compounds that can come from multiple sources.

Straight gas chromatography (GC) is not a suitable alternative for analyzing the peroxide products of alkene–O<sub>3</sub> reactions, because the labile peroxide bond thermally decomposes at the high temperatures required for analysis of compounds containing more than a few carbon atoms. A few years ago, however, Turnipseed et al. [7] demonstrated that high molecular mass hydroperoxides could be analyzed by GC–MS through the use of pre-column trimethylsilyl (TMS) derivatization to form stable TMS hydroperoxide derivatives. This method has apparently not been applied to the analysis of hydroperoxides of environmental importance, in spite of its potential utility. We report here the successful application of this technique to the analysis of a different class of hydroperoxides than was previously investigated, and demonstrate its use for the study of mechanisms of alkene–O<sub>3</sub> reactions. Specifically, we applied this technique to the analysis of  $\alpha$ -methoxyalkyl hydroperoxides formed in the gas- and liquid-phase reactions of terminal alkenes with O<sub>3</sub> in the presence of methanol (CH<sub>3</sub>OH) (an SCI-scavenger).

## 2. Experimental

### 2.1. Chemicals

Cumene hydroperoxide (CMOOH) ( $\alpha,\alpha'$ -dimethylbenzyl hydroperoxide) (80%), 1-octene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH=CH<sub>2</sub>] (98%), 1-nonene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CH=CH<sub>2</sub>] (98%), 1-decene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH<sub>2</sub>] (94%), 1-dodecene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>CH=CH<sub>2</sub>] (95%), 1-tetradecene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>CH=CH<sub>2</sub>] (92%), *n*-hexadecane (>99%), acetaldehyde (99.5%), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) (97%), and bis(trimethylsilyl)trifluoroacetamide (BSTFA) (>99%) were all purchased from Sigma–Aldrich (Milwaukee, WI, USA), and 2-methyl-1-octene [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>C(CH<sub>3</sub>)=CH<sub>2</sub>] (99%) from ChemSampCo (Trenton, NJ, USA). Optima grade methanol and ethyl acetate were obtained from Fisher Scientific (Tustin, CA, USA). The 18 M $\Omega$  water was generated using a Barnstead (Dubuque, IA, USA) NANOpure pure water filtration system and O<sub>3</sub> was generated using a Welsbach (El Sobrante, CA, USA) T-408 ozone generator. All chemicals were used without further purification.

### 2.2. Equipment

A Hewlett–Packard (HP) 6890 GC system (Palo Alto, CA, USA) equipped with an HP-1701 fused-silica capillary column (30 m  $\times$  0.53 mm with a 1.0  $\mu$ m film thickness) and a FID system was used for quantitative analysis. A HP 5890 GC system equipped with an identical column and 5971A mass-selective detector was used to identify

TMS-hydroperoxide derivatives and other compounds. The same method was used for both instruments: a split/splitless injection inlet set at 220 °C was used in the splitless mode, an initial column temperature of 50 °C was maintained for 8 min and was subsequently ramped at 10 °C min<sup>-1</sup> to a final temperature of 280 °C, and the FID and GC–MS transfer line were maintained at 280 °C. Use of identical columns and methods provided a direct correspondence between chromatograms obtained with the two systems.

### 2.3. Cumene hydroperoxide derivatization

A solution containing equimolar concentrations of cumene hydroperoxide and *n*-hexadecane (an internal reference (IR)) in ethyl acetate was used to prepare standard solutions (cumene hydroperoxide concentrations: 3800, 760, 380, 76, and 7.6 mg l<sup>-1</sup>) by serial dilution. Ten microlitres of MSTFA derivatizing reagent was added to each standard, and an additional 30 µl was added to those with cumene hydroperoxide concentrations >1000 mg l<sup>-1</sup> to ensure excess derivatizing reagent. One set of standards was derivatized at room temperature for 24 h, while another set was first immersed in 40 °C water for 1 h before standing at room temperature for the remainder of the 24 h period. Both sets of standards were analyzed by GC–FID. Derivatization efficiencies were calculated relative to the IR using FID effective carbon number (ECN) calculations as described by Scanlon and Willis [8].

### 2.4. Liquid-phase ozonolysis of alkenes in methanol

Individual solutions of 1-octene, 1-nonene, 2-methyl-1-octene, 1-decene, 1-dodecene, and 1-tetradecene were prepared by adding 7.0 ± 0.1 mg each of alkene and IR to a glass bubbler containing 25 ml of methanol. Two percent O<sub>3</sub> in O<sub>2</sub> was then bubbled through the solution at 1 l min<sup>-1</sup> for 6–8 s (~10<sup>-4</sup> moles of O<sub>3</sub>). After reaction, the methanol was evaporated using a stream of N<sub>2</sub>, the residue was re-dissolved in 4 ml of ethyl acetate, and 20 µl of MSTFA was added to each solution. After standing at room temperature for 24 h, solutions were analyzed by GC–FID and GC–MS.

### 2.5. Gas-phase reactions of alkenes with O<sub>3</sub> in the presence of methanol

Gas-phase reactions of alkenes with O<sub>3</sub> were conducted at atmospheric pressure (~9.9 × 10<sup>4</sup> Pa) and room temperature (25 ± 3 °C) in a 70001 PTFE film environmental chamber filled with air [<5 ppb (v/v) (ppbv) hydrocarbons, <0.5% relative humidity (RH)] from an Aadco (Cleveland, OH, USA) clean air system. In all reactions, measured quantities of the alkene (3.5–4.4 ppmv) and methanol (2.5 × 10<sup>4</sup> ppmv) were added to the chamber by evaporation into a stream of clean air prior to adding O<sub>3</sub>. The concentration of methanol was sufficiently high relative to the alkene to allow methanol to out-compete all other species (with

formaldehyde, a co-product of terminal alkene ozonolysis, being the major competitor) for reaction with SCIs. Rates of SCI reactions with methanol relative to formaldehyde,  $R_{\text{SCI}}$ , were calculated using the following equation:

$$R_{\text{SCI}} = \frac{k_{\text{SCI,MeOH}}[\text{MeOH}]}{k_{\text{SCI,HCHO}}[\text{HCHO}]} \quad (1)$$

where  $k_{\text{SCI,MeOH}}/k_{\text{SCI,HCHO}}$  is the rate-constant ratio for reaction of a SCI with methanol relative to formaldehyde and [MeOH] and [HCHO] are the gas-phase concentrations of methanol and formaldehyde, respectively. The rate-constant ratio was assumed to be the same for all reactions and equal to the value (8.1 × 10<sup>-3</sup>) measured for C<sub>13</sub> SCI formed from reaction of 1-tetradecene with O<sub>3</sub> [9]. Assuming [HCHO] ~1.3 ppmv (50% yield from reaction R1a), gives  $R_{\text{SCI}} \sim 160$ . The methanol also scavenged ≥99% of OH radicals formed in each reaction [10].

Chamber reactions were conducted with excess alkene relative to O<sub>3</sub>. Alkene concentrations were as follows (in ppmv): 1-octene (4.4 ± 0.1), 1-nonene (4.0 ± 0.1), 2-methyl-1-octene (4.0 ± 0.1), 1-decene (3.5 ± 0.1), 1-dodecene (3.7 ± 0.1), and 1-tetradecene (3.8 ± 0.1). Reactions were initiated by flushing O<sub>3</sub> into the chamber using clean air. Initial O<sub>3</sub> mixing ratios of 2.5 ± 0.3 ppmv were achieved in the chamber for each reaction. A PTFE-coated fan was run during all additions to ensure rapid mixing. O<sub>3</sub> concentrations were measured continuously using a Dasibi (Glendale, CA, USA) model 1030-AH O<sub>3</sub> monitor, and reactions were allowed to proceed until the O<sub>3</sub> concentration was <0.2 ppmv before collecting samples. The amount of alkene consumed during each reaction was assumed to be equal to the amount of O<sub>3</sub> consumed. No O<sub>3</sub> was consumed when only methanol was present. This approach was verified in a few experiments by analyzing alkene concentrations before and after reaction. For these measurements, 100 ml of chamber air was sampled onto solid Tenax TA adsorbent and analyzed immediately by GC–FID. The Tenax TA samples were placed in a split/splitless inlet that was run in the splitless mode. The inlet was initially at room temperature, and then ramped to 250 °C at a rate of ~23 °C min<sup>-1</sup> after inserting the sample tube. The FID response was compared with standard calibrations to determine alkene concentrations.

At the end of each reaction, particle and gas samples were collected in parallel from the chamber for 90 min using a particle filter and an impinger apparatus. For the reaction of alkenes having ≥10 carbons, an additional particle filter was placed directly upstream of the impinger to avoid potential capture of particle-associated products in the impinger. Filter samples were collected on Millipore (Bedford, MA, USA) 0.45 µm pore size, Fluoropore FHLF, 47 mm filters at a volume flow rate of 14.7 l min<sup>-1</sup>. The impinger was designed and assembled in our laboratory and operated at a volume flow rate of 4.5 l min<sup>-1</sup>. The main body of the impinger is a 25 cm long × 5.5 cm o.d. cylindrical glass vessel with a capacity of ~600 ml. The top of the vessel is sealed with a rubber stopper through which two inlet tubes and an outlet tube

(all 0.635 cm o.d. PTFE) pass. The end of each inlet tube is plugged with a metal diffusion stone to generate bubbles as the chamber air enters the impinger solvent. Prior to sampling, 150 ml of ethyl acetate and  $4.0 \times 10^{-5}$  g *n*-hexadecane were added to the impinger. In order to minimize the loss of ethyl acetate and volatile sample species, the impinger was packed in ice during sampling. Sampling flows were fixed by critical orifices located between the samplers and a vacuum pump and by the pressure drops across the samplers. Flows were measured using a calibrated gas meter.

At the end of the sampling period, filters were spiked with  $4.0 \times 10^{-5}$  g of *n*-hexadecane and suspended in 10 ml of ethyl acetate. The *n*-hexadecane was added to the impinger and filter samples to evaluate compound recovery and as the IR for ECN calculations following GC analysis. Filter samples were extracted overnight at  $\sim 20^\circ\text{C}$ . Immediately following sample collection, the impinger solution was transferred to a 500 ml Erlenmeyer flask and the impinger was rinsed twice with 10 ml of ethyl acetate. The rinse solutions were added to the original impinger solution and stored overnight at approximately  $-20^\circ\text{C}$ . The following day, filters were removed from solution and rinsed four times with 2 ml of ethyl acetate, and the rinse solutions were added to the original filter solution. Flasks containing the impinger samples and filter extracts were packed in ice and the samples were evaporated to dryness under vacuum. The residue in each flask was then redissolved in 2 ml of ethyl acetate, and the 2 ml samples were split into 1 ml aliquots for hydroperoxide analysis by MSTFA derivatization and carboxylic acid analysis by on-line BSTFA derivatization.

As a check on possible evaporative loss of reaction products during the evaporation of solvent from gas-phase reaction samples, underivatized and derivatized products of the solution reaction of 1-octene (the most volatile alkene studied) in methanol were analyzed before and after solvent evaporation. Solution reactions were used because product concentrations were high enough for analysis without evaporating the solvent. The exact procedure that was used for evaporating solvent from the gas-phase reaction samples (solvent evaporation under vacuum while the samples were maintained at  $0^\circ\text{C}$ ) was used to evaporate the solvent from each liquid reaction solution. No significant differences were observed in the concentrations of methyl octanoate (an ester that is the major decomposition product of  $\alpha$ -methoxyheptyl hydroperoxide, as discussed below) in the underivatized samples, or in the concentrations of the TMS- $\alpha$ -methoxyheptyl hydroperoxide derivative in the derivatized samples. Because these are the most volatile compounds of interest in this study, volatilization losses should not be a problem in our analyses. It is important to note, however, that some of the aldehyde products of these reactions are more volatile and can be lost during solvent evaporation.

The MSTFA derivatization procedure for impinger and filter samples was the same as that described above for the liquid-phase reactions (Section 2.4). Components were identified by comparing retention times with those of authen-

tic standards synthesized in the methanol solution reactions (the identities of which had been verified by GC-MS), and were quantified by GC-FID using ECN calculations measured against the IR. Carboxylic acids were analyzed by an on-line BSTFA derivatization procedure we have reported previously [11]. Briefly, BSTFA and the reaction solution are co-injected into the hot ( $220^\circ\text{C}$ ) inlet of the GC system, where derivatization occurs in the gas-phase. The carboxylic acids were identified by comparing retention times with those of authentic commercial standards analyzed by the same method, and were quantified by GC-FID using ECN calculations measured against the IR.

### 3. Results and discussion

When Turnipseed et al. [7] developed their pre-column derivatization procedure based on the formation of stable TMS hydroperoxide derivatives, they used the technique to analyze hydroperoxides in biological matrices. Specifically, 2,6-di-*tert*-butyl-4-hydroperoxy-4-methylcyclohexadienone and 2,4,6-trimethyl-4-hydroperoxycyclohexadienone from liver samples were quantified following off-line derivatization by MSTFA. Authentic standards were synthesized in order to develop standard calibration curves for quantification. We have taken a simpler and less time consuming approach to quantify  $\alpha$ -methoxyalkyl hydroperoxides by employing the FID effective carbon number concept.

The ECN concept was originally introduced to explain observed FID responses obtained from the analysis of a variety of organic compounds [12]. This concept has since been applied to column evaluation, to calculate response factors for compounds that cannot be obtained in pure form, and as a check on experimentally determined response factors for neat and derivatized compounds [8]. Because experimentally determined response factors are dependent on the completeness of reaction when a derivatization step is required, it is necessary to first determine the efficiency of hydroperoxide derivatization by MSTFA before using ECN calculations to quantify compounds for which independent calibrations cannot be developed. Here, we apply the ECN concept to: (1) determine the efficiency of hydroperoxide derivatization by MSTFA and (2) quantify the yield of  $\text{C}_{n-1}$   $\alpha$ -methoxyalkyl hydroperoxides as a measure of the yield of  $\text{C}_{n-1}$  SCI formed from gas-phase alkene ozonolysis.

A detailed discussion of the ECN concept and related calculations are presented elsewhere [8]. The basic principle of the ECN concept is that maximum FID response is achieved for the analysis of alkanes and predictably diminishes as alkyl hydrogens are replaced by constituents such as oxygen. Due to predictable FID response, alkanes are generally used as an IR for ECN calculations. *n*-Hexadecane was chosen as the IR for this study due to its predictable response and because it did not co-elute with any products of interest. The FID response to a non-alkane compound relative to that of the chosen IR is then used to experimentally determine its

ECN ( $ECN_{exp}$ ). If equimolar concentrations of IR and the compound of interest are present in solution,  $ECN_{exp}$  can be calculated as follows:

$$ECN_{exp} = \frac{FID\ response_{compound}}{FID\ response_{IR}} \times ECN_{IR} \quad (2)$$

where  $ECN_{IR}$  is the ECN of the IR compound. The derivatization efficiency (DE) is then the ratio of  $ECN_{exp}$  to the ECN calculated using tabulated contributions ( $ECN_{theory}$ ):

$$DE = \frac{ECN_{exp}}{ECN_{theory}} \quad (3)$$

The contribution of different functional groups to  $ECN_{theory}$  is well established [8].  $ECN_{theory}$  is the sum of contributions from each carbon atom in the compound with corrections made for functional groups. Aliphatic and aromatic carbons each contribute one unit to  $ECN_{theory}$ , so the  $ECN_{theory}$  of alkanes is simply the total number of carbon atoms (e.g.,  $ECN_{theory} = 16$  for *n*-hexadecane). To calculate  $ECN_{theory}$  for oxygenated and derivatized compounds in this study, we used the functional group contributions of Scanlon and Willis when applicable. To our knowledge, the contribution of TMS hydroperoxide derivatives to  $ECN_{theory}$  has not been reported. On the basis of its structural similarity to a TMS carboxylic acid derivative [ $-C(O)OTMS$ ], which is listed in Scanlon and Willis, we therefore assumed a contribution of three units. The  $ECN_{theory}$  for the TMS cumene hydroperoxide derivative (CMOOTMS) is then 11 (i.e., eight units from aromatic or aliphatic carbons plus three units from [ $-COOTMS$ ]). This contribution was also applied to calculate  $ECN_{theory}$  for all  $\alpha$ -methoxyalkyl hydroperoxides investigated in this study.

### 3.1. Efficiency of hydroperoxide derivatization by MSTFA

The efficiency of hydroperoxide derivatization by MSTFA was determined using commercially available cumene hydroperoxide. Chromatograms of CMOOH analyzed prior to and following MSTFA derivatization are shown in Fig. 1A and B, respectively. The only peaks present in the absence of MSTFA derivatization are from the IR and, possibly, decomposition products of underivatized CMOOH. An additional peak appears in the chromatogram following MSTFA derivatization, which GC–MS analysis confirmed is CMOOTMS. The CMOOTMS peak in the chromatogram is well defined with no tailing. The mass spectrum of CMOOTMS is shown in Fig. 2 and is similar to the previously published spectrum of this compound [7]. Fragmentation occurs primarily at the C–OO bond, which is consistent with the fragmentation of CMOOH and other organic hydroperoxides we have analyzed previously in our lab using thermal desorption particle beam mass spectrometry [13]. For CMOOTMS, fragmentation results in a base peak at  $m/z = 119$  [ $C_9H_{11} = M - 105$ ] $^{•+}$  due to loss of  $OOSi(CH_3)_3$  from the molecular ion. A smaller peak is also present at  $m/z = 105$ , which apparently has contributions from [ $OOSi(CH_3)_3$ ] $^{•+}$

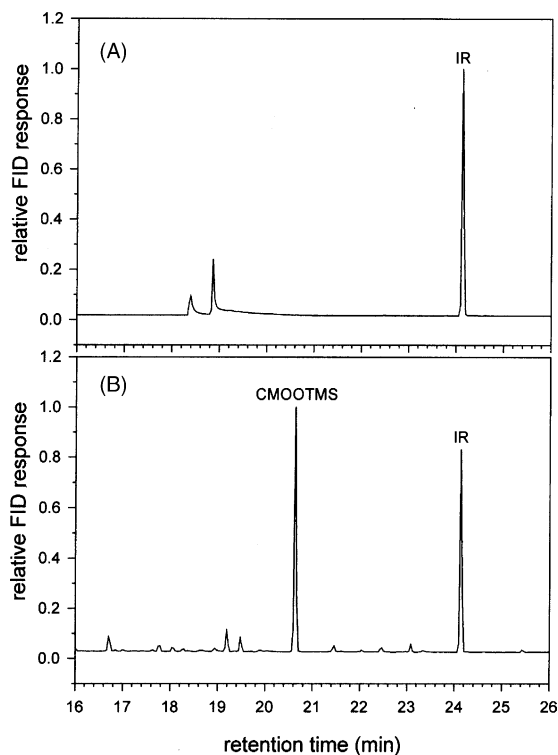


Fig. 1. Chromatograms of cumene hydroperoxide solutions: (A) derivatized and (B) after MSTFA derivatization. The peak labeled IR corresponds to the internal reference alkane, *n*-hexadecane.

and from [ $C_8H_9$ ] $^{•+}$  (it is also present in the mass spectrum of CMOOH). As will be confirmed below, the presence of a large peak at [ $M - 105$ ] $^{•+}$  and a smaller fragment at  $m/z = 105$  are characteristic of TMS hydroperoxide derivatives.

Efficiencies for CMOOH derivatization at room temperature are shown in Fig. 3. Efficiencies were >90% over most of the concentration range, but decreased to ~50% at the lowest concentration of  $7.6\ mg\ l^{-1}$ . The error bars represent one standard deviation of the mean for four replicate GC measurements. These results demonstrate the high accuracy and precision with which otherwise thermally labile hydroperoxides can be analyzed using off-line derivatization by MSTFA. It is worth noting that, although Turnipseed et al. [7] derivatized samples at  $40\ ^\circ C$ , we measured similar derivatization efficiencies at  $40\ ^\circ C$  and at room temperature. We therefore performed our procedure at room temperature and used samples with sufficiently high hydroperoxide concentrations to achieve derivatization efficiencies >90%.

### 3.2. GC analysis of the products of reactions of terminal alkenes with $O_3$ in methanol solution

A number of studies have shown that  $\alpha$ -alkoxyalkyl hydroperoxides are formed with yields close to unity when terminal alkenes are reacted with  $O_3$  in an alcohol solution [14–16]. This method therefore provides a simple means for synthesizing  $\alpha$ -alkoxyalkyl hydroperoxides for

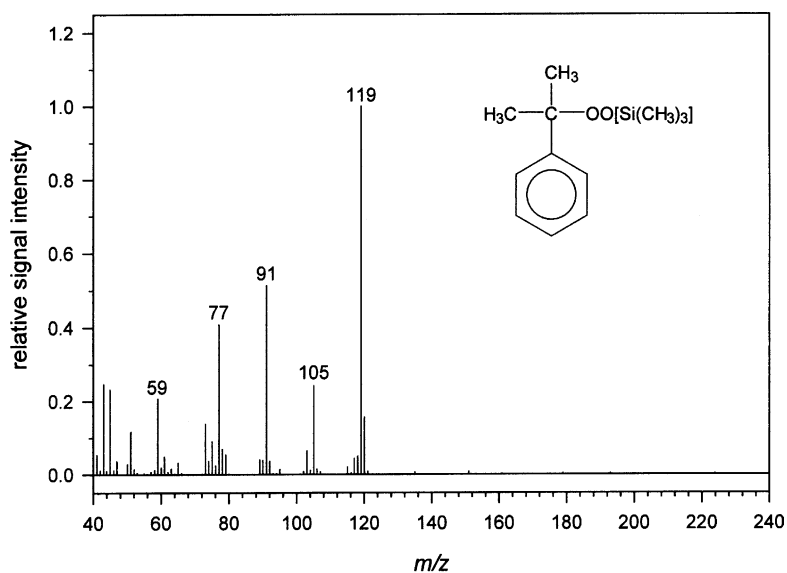


Fig. 2. Mass spectrum of the TMS cumene hydroperoxide derivative (CMOOTMS).

use as mass spectral standards, as we have done in previous investigations of aerosol chemistry [9,13]. In the present study, we analyzed  $\alpha$ -methoxyalkyl hydroperoxides produced in methanol solution reactions of 1-octene, 1-decene, 1-dodecene, and 1-tetradecene and their MSTFA derivatives in order to characterize the mass spectral and chromatographic properties of these compounds.

GC–FID chromatograms for the reaction of 1-decene are presented in Fig. 4A and B. The chromatogram of the underivatized solution (Fig. 4A) is characterized by three peaks representing, in order from shortest to longest retention time: nonanal, methyl nonanoate, and *n*-hexadecane, as verified by GC–MS. As with cumene hydroperoxide, an additional peak appears in the chromatogram following MSTFA derivatiza-

tion (Fig. 4B). Similar results were seen for the 1-octene, 1-dodecene, and 1-tetradecene reactions. Mass spectra of the compounds that appear only after MSTFA derivatization are shown in Fig. 5A–D. They are all characterized by a large fragment peak at  $[M - 105]^{\bullet+}$  and a smaller peak at  $m/z = 105$ . Based on similarities with the mass spectrum of CMOOTMS, these compounds are identified as  $C_{n-1}$  TMS  $\alpha$ -methoxyalkyl hydroperoxide derivatives. The  $C_{n-1}$  aldehydes are expected products from primary ozonide decomposition (reaction R1b), and the  $C_{n-1}$  methyl esters are most likely formed by dehydration of the  $\alpha$ -methoxyalkyl hydroperoxides according to the reaction:

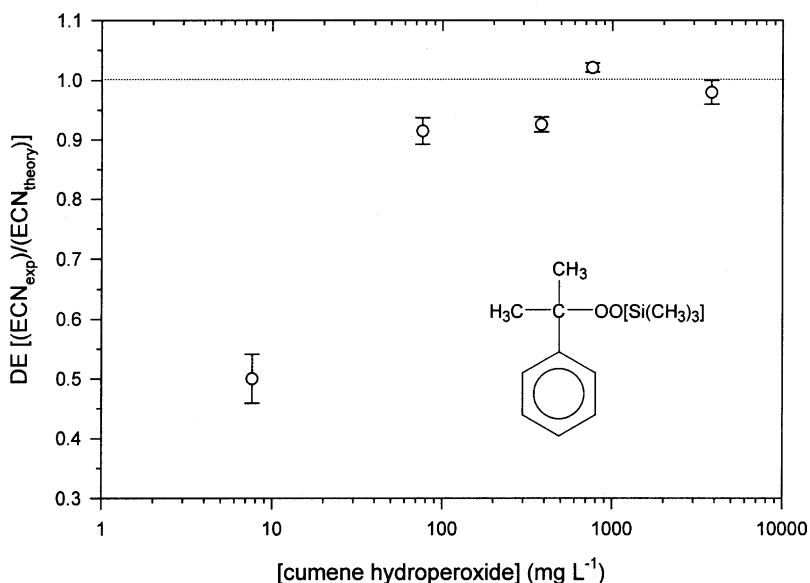


Fig. 3. Derivatization efficiency (DE) of cumene hydroperoxide. Error bars represent one relative standard deviation of DE for replicate GC analyses.

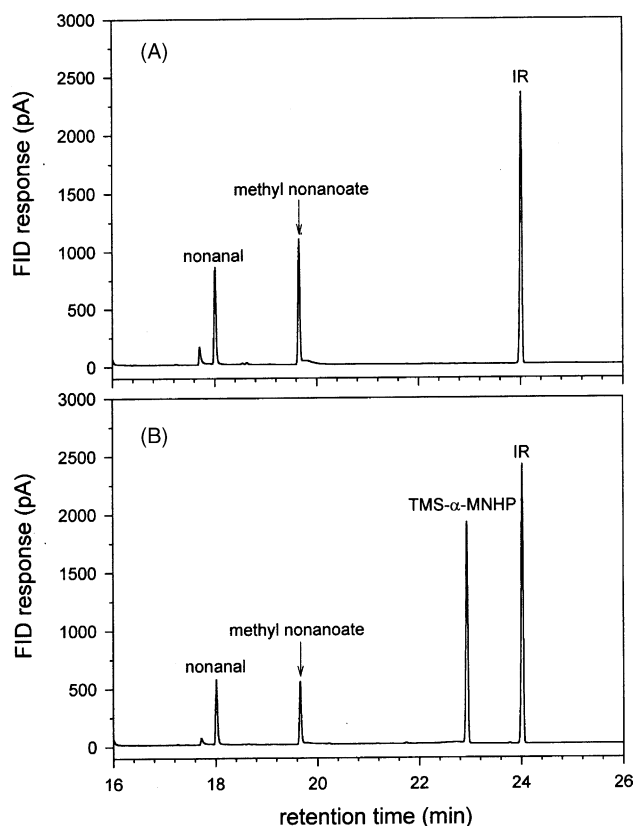


Fig. 4. Chromatograms of ozonized solutions of 1-decene in methanol: (A) underderivatized and (B) after MSTFA derivatization. The peak labeled TMS- $\alpha$ -MNHHP corresponds to the trimethylsilyl derivative of  $\alpha$ -methoxynonyl hydroperoxide.

Dehydration probably occurs during derivatization or GC analysis, since the  $C_{13}$  methyl ester was not observed when the products of either the gas- or liquid-phase reactions of 1-tetradecene in methanol were analyzed by thermal desorption particle beam mass spectrometry: only the  $C_{13}$   $\alpha$ -methoxyalkyl hydroperoxide was present [9,13]. Furthermore, results from a recent computational study have shown these types of compounds to be quite stable, so that decomposition at room temperature would require catalysis [17]. Regardless of when decomposition occurs, however, for SCI quantitation the  $C_{n-1}$   $\alpha$ -methoxyalkyl hydroperoxide and methyl ester must both be treated as products of methanol-SCI reactions. In the results presented here,  $C_{n-1}$  SCI yields were calculated as the sum of the  $C_{n-1}$   $\alpha$ -methoxyalkyl hydroperoxide and  $C_{n-1}$  methyl ester yields.

### 3.3. Yields of $C_{n-1}$ SCIs from gas-phase reactions of terminal alkenes with $O_3$ in the presence of methanol

#### 3.3.1. 1-Octene, 1-nonene, and 2-methyl-1-octene

The calculated yields of  $C_{n-1}$  SCIs and the measured yields of  $C_{n-1}$   $\alpha$ -methoxyalkyl hydroperoxides and  $C_{n-1}$  methyl esters that were used for the calculations are reported

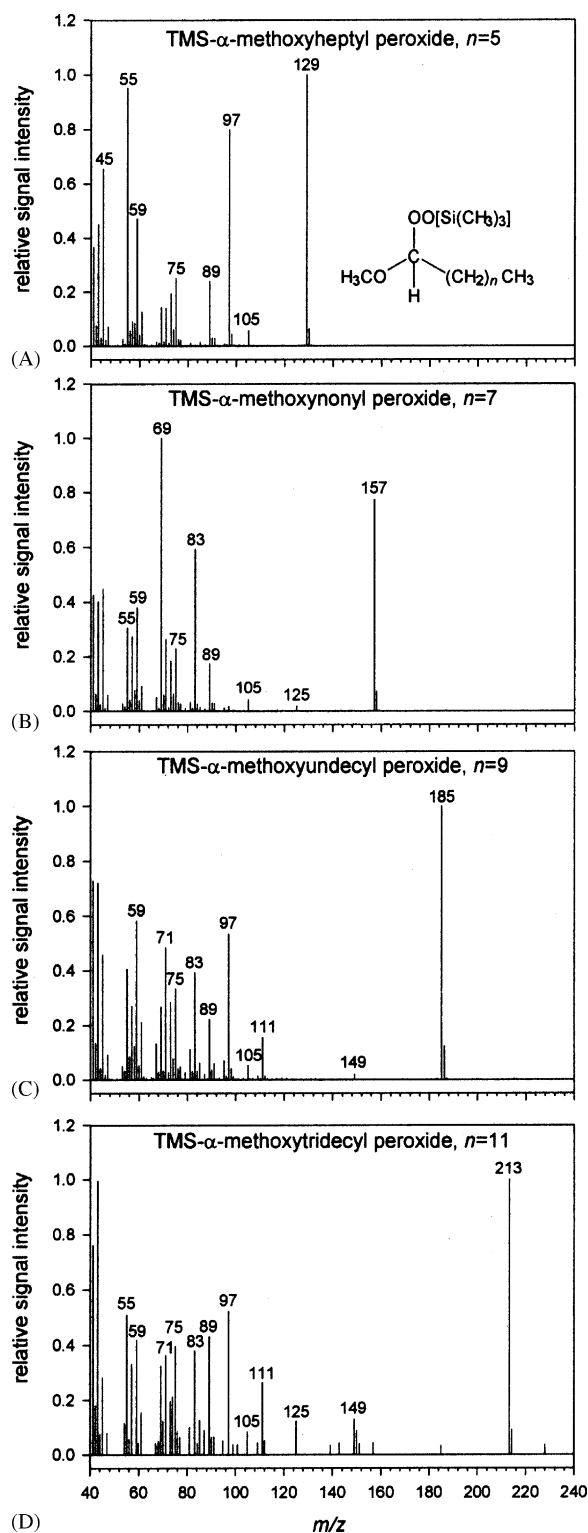


Fig. 5. Mass spectra of TMS derivatives of  $\alpha$ -methoxyheptyl, nonyl, undecyl, and tridecyl hydroperoxides formed in liquid-phase ozonolysis of 1-octene, 1-decene, 1-dodecene, and 1-tetradecene, respectively, in methanol.

Table 1

Yields of  $C_{n-1}$  methyl esters,  $\alpha$ -methoxy hydroperoxides, and stabilized Criegee intermediates (SCIs) from gas-phase ozonolysis of alkenes in the presence of methanol SCI scavenger

Alkene	Reference	Product	Product yield	$C_{n-1}$ SCI yield
1-Octene	[6]	$\alpha$ -Hydroxyheptyl hydroperoxide <sup>a</sup>	0.23	0.23
		Hydroxymethyl hydroperoxide	0.12	
	This study	Methyl heptanoate	$0.04 \pm 0.02$	$0.20 \pm 0.07$
		$\alpha$ -Methoxyheptyl hydroperoxide	$0.16 \pm 0.08$	
1-Nonene	This study	Methyl octanoate	$0.02 \pm 0.01$	$0.20 \pm 0.03$
		$\alpha$ -Methoxyoctyl hydroperoxide	$0.18 \pm 0.04$	
2-Methyl-1-octene	This study	$\alpha$ -Methyl- $\alpha'$ -methoxyoctyl hydroperoxide	$0.29 \pm 0.01$	$0.29 \pm 0.01$

All yields presented are relative to amount of reacted alkene.

<sup>a</sup> Measured as  $(\Delta[\text{H}_2\text{O}_2] + \Delta[\text{heptanal}])/2$  between reactions conducted under dry and humid conditions.

in Table 1 for chamber reactions of 1-octene, 1-nonene, and 2-methyl-1-octene. Results for similar reactions conducted with 1-decene, 1-dodecene, and 1-tetradecene are discussed below. The yields of  $C_{n-1}$  SCIs from the reactions of 1-octene and 1-nonene were both 0.20. These values are in good agreement with the  $C_{n-1}$  SCI yield of 0.23 determined by Hasson et al. [5] for 1-octene calculated as the average of the change in  $[\text{H}_2\text{O}_2]$  and  $[C_{n-1}$  carbonyl] between reactions under dry ( $<0.5\%$  RH) and humid ( $>50\%$  RH) conditions. SCI yields for the reaction of 1-nonene have not been measured previously, but total SCI ( $C_{n-1} + C_1$ ) yields reported by Hasson et al. [5] for 1-butene (0.27), 1-pentene (0.29), and 1-octene (0.35) indicate a small increase in the yield of  $\sim 0.02$  per carbon atom.

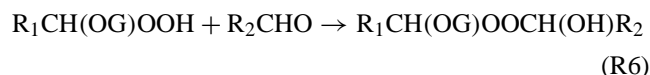
The  $C_{n-1}$  SCI yield measured for the reaction of 2-methyl-1-octene was 0.29. This value was calculated solely from the yield of  $\alpha$ -methyl- $\alpha'$ -methoxyoctyl hydroperoxide, because no  $C_{n-1}$  methyl ester was observed among the reaction products. The absence of methyl octanoate is probably due to the lack of a  $\alpha$ -hydrogen in  $\alpha$ -methyl- $\alpha'$ -methoxyoctyl hydroperoxide, which apparently is necessary for ester formation by dehydration (reaction R5). The yield of the  $C_{n-1}$  SCI is  $\sim 50\%$  higher for 2-methyl-1-octene than for 1-octene and 1-nonene. One reason for this may be that the primary ozonide formed from 2-methyl-1-octene preferentially decomposes to form the more substituted excited CI with  $>0.5$  yield. Although the yields of the  $C_{n-1}$  and  $C_1$  excited CIs are both 0.5 for unsubstituted terminal alkenes (at least in the  $3 \leq n \leq 10$  range studied to date), measurements made on a few 2-methyl-1-alkenes indicate that yields of the more substituted excited CIs are  $\sim 0.6$ – $0.8$  [3]. Assuming that the fraction of excited CIs that become stabilized, ( $C_{n-1}$  SCI)/( $C_{n-1}$  CI), is the same for 2-methyl-1-octene as for 1-octene or 1-nonene, and is therefore equal to  $0.2/0.5 = 0.4$ , then a  $C_{n-1}$  excited CI yield of 0.72 would lead to a  $C_{n-1}$  SCI yield of 0.29.

### 3.3.2. 1-Decene, 1-dodecene, and 1-tetradecene

On the basis of the trend observed by Hasson et al. [5], that the SCI yield increases by  $\sim 0.02$  per carbon atom,

the SCI yields from reactions of 1-decene, 1-dodecene, and 1-tetradecene would be expected to be slightly higher than those from the reactions of 1-octene and 1-nonene. In a previous study using our thermal desorption particle beam mass spectrometer to quantify  $\alpha$ -methoxytridecyl hydroperoxide in aerosol formed from the ozonolysis of 1-tetradecene in the presence of methanol, the  $C_{13}$  SCI yield was between 0.23 and 0.26 [9]. The SCI  $C_{n-1}$  yields measured here were much lower than expected: 0.065, 0.063, and 0.062 from reaction of 1-decene, 1-dodecene, and 1-tetradecene, respectively.

The remarkably low SCI yields measured for these alkenes are probably due to an analytical artifact, caused by reaction of a large fraction of the  $\alpha$ -methoxyalkyl hydroperoxides with aldehydes (produced in reactions R1a and R1b) to form peroxyhemiacetals according to the reaction:



Peroxyhemiacetals are not analyzed by our method. This reaction is well known from solution studies [18] and also was observed to occur (apparently on particle surfaces) over a few hours in our studies of aerosol formation from 1-tetradecene ozonolysis [13]. In the present case, this reaction most likely occurred during sample collection and preparation because, at least in the 1-decene reaction, little aerosol was formed. Particulate  $\alpha$ -methoxyalkyl hydroperoxides are collected on the filter and exposed to aldehydes throughout the sampling period, whereas the volatile  $\alpha$ -methoxyalkyl hydroperoxides are collected with aldehydes in the impinger solution and then concentrated during solvent evaporation. Both these scenarios allow ample opportunity for reaction. In the case of reactions of alkenes smaller than 1-decene, GC analysis has indicated that most of the  $C_{n-1}$  aldehydes are lost during solvent evaporation because of their higher volatility.

To further test this explanation for the low SCI yields, we repeated the 1-octene solution reaction and then split the solution in half. Both solutions were then processed as before (Section 2.5), except that after evaporating the



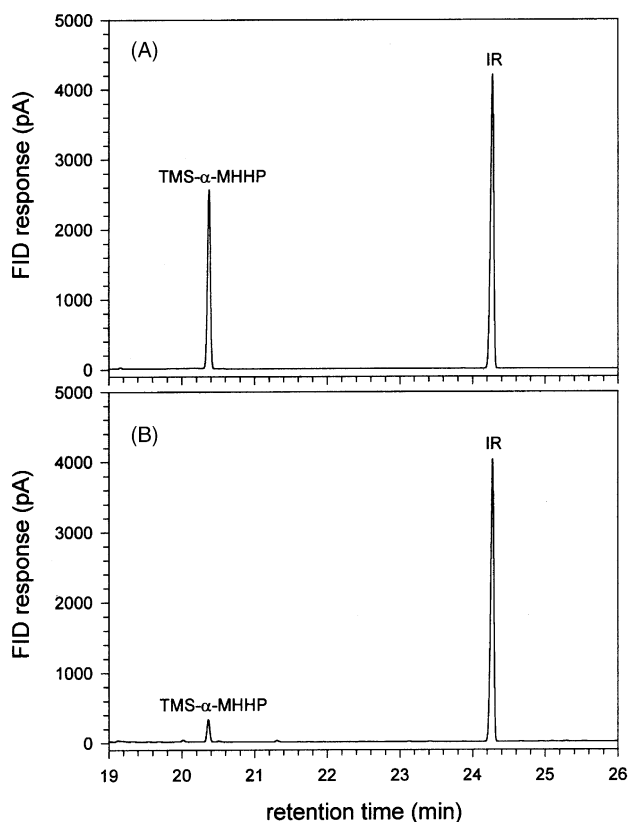


Fig. 6. Chromatograms from 1-octene liquid-phase ozonolysis reaction showing the potential formation and effect of peroxyhemiacetal formation on the analysis of  $\alpha$ -methoxyalkyl hydroperoxides. Following ozonolysis, the resulting solution was divided into two volumes. The chromatogram (A) is from analysis of reaction solution that was immediately derivatized by MSTFA and (B) is from a solution to which acetaldehyde was added, allowed to stand at  $0^\circ\text{C}$  for  $\sim 30$  min, and subsequently evaporated prior to MSTFA derivatization. The peak representing the trimethylsilyl derivative of  $\alpha$ -methoxyheptyl hydroperoxide has been denoted TMS- $\alpha$ -MHHP.

methanol, one sample was first dissolved in  $\sim 2$  ml of acetaldehyde and allowed to stand at  $0^\circ\text{C}$  for 30 min, after which time the acetaldehyde was evaporated and the processing completed. The GC-FID chromatograms of these samples are shown in Fig. 6A and B. Although peaks due to the TMS  $\alpha$ -methoxyheptyl hydroperoxide derivative are present in the chromatograms of both samples, the intensity is much lower in the sample to which acetaldehyde was added (Fig. 6B), apparently because of peroxyhemiacetal formation. No change was observed in the methyl ester peak, and no new peak appeared to indicate the presence of the peroxyhemiacetal.

Although we have not identified peaks that clearly come from peroxyhemiacetals in any reaction, we have observed broad humps near the methyl ester peak in the chromatograms of MSTFA-derivatized samples from ozonolysis of  $n \geq 10$  alkenes. For example, Fig. 7 shows chromatograms for the 1-tetradecene filter sample before (Fig. 7A) and after (Fig. 7B) MSTFA addition. Prior to derivatization, there is a relatively narrow shoulder to the

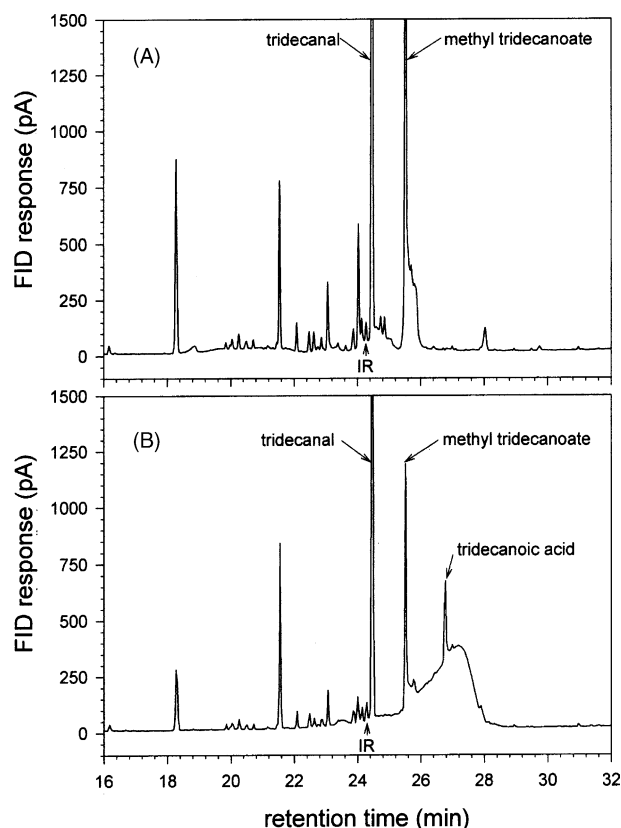


Fig. 7. Chromatograms from analysis of filter samples collected following gas-phase ozonolysis of 1-tetradecene in the presence of methanol. Chromatogram (A) is from analysis of underivatized sample and (B) is from analysis of the same sample following derivatization by MSTFA.

immediate right of the methyl tridecanoate peak, which could represent methyl tridecanoate formed by peroxyhemiacetal decomposition on the column. After derivatization, the shoulder decreases in intensity and a broad hump appears beneath the tridecanoic acid peak. The broad hump could be from derivatized products of peroxyhemiacetal decomposition (e.g., acids) that do not come off the column in the absence of MSTFA. Similar results were seen for the 1-decene and 1-dodecene reactions, but with a decreased intensity of the unresolved hump. These results do not confirm the presence of peroxyhemiacetals. They do, however, suggest that for  $n \geq 10$  alkenes a large portion of the mass formed from SCI reactions is converted to unidentified species that may be peroxyhemiacetals.

Attempts to remove aldehydes during sampling or by derivatization in order to eliminate the formation of peroxyhemiacetals were unsuccessful. In one experiment, the carbonyl derivatizing reagent 2,4-dinitrophenylhydrazine (DNPH) [19] was added to the impinger solution containing the products of the 1-decene ozonolysis reaction before processing. In another experiment, a pair of laboratory-built charcoal denuders (also called diffusion dryers) was placed upstream of the filter used to collect particle products of the 1-tetradecene ozonolysis reaction in order to remove volatile

Table 2  
Yields of  $C_{n-1}$  carboxylic acids from gas-phase ozonolysis of alkenes in the presence of methanol SCI scavenger

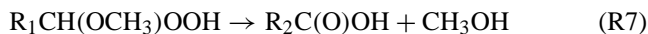
Alkene	$C_{n-1}$ carboxylic acid	Yield (%)
1-Octene	Heptanoic acid	$2.2 \pm 0.9$
1-Nonene	Octanoic acid	$2.2 \pm 0.8$
1-Decene	Nonanoic acid	$1.0 \pm 0.6$
1-Dodecene	Undecanoic acid	$1.5 \pm 0.1$
1-Tetradecene	Tridecanoic acid	$2.5 \pm 0.8$

All yields are reported relative to amount of reacted alkene.

aldehydes (but not particles) by adsorption. Each denuder consists of two concentric cylinders, with the outer one being a copper pipe (5.0 cm i.d.; 30.5 cm length) and the inner one a fine wire mesh screen (1.3 cm i.d.; 30.0 cm length). The annular region is filled with charcoal which adsorbs volatile organics as the aerosol flows through the wire mesh cylinder. Particles diffuse too slowly to be removed. Neither of these procedures was successful, as GC-FID analysis confirmed the presence of significant  $C_{n-1}$  aldehyde concentrations and  $\alpha$ -methoxyalkyl hydroperoxide yields were similar to those measured previously. The DNPH approach likely failed because the procedure is normally performed in acidic solution, which was not possible here because of the potential for acid-catalyzed hydroperoxide decomposition. The denuder approach probably failed because the necessary sampling flow rates were too high to efficiently remove the aldehydes. Subsequent evaluation of the denuders revealed that they removed only  $\sim 30\%$  of gas-phase cyclohexane ([cyclohexane]  $\sim 1000$  ppmv) at the high flow rates ( $\sim 151 \text{ min}^{-1}$  rather than the typical  $11 \text{ min}^{-1}$ ) used in this study for collecting filter samples. With additional development, however, one or both of these methods could be successful.

### 3.4. Yields of $C_{n-1}$ carboxylic acids from gas-phase reactions of terminal alkenes with $O_3$ in the presence of methanol

Impinger and filter samples from the alkene- $O_3$  chamber reactions were also analyzed for  $C_{n-1}$  carboxylic acids using an on-line, inlet-based BSTFA derivatization method we reported previously [11]. These data provide an estimate of the extent to which  $\alpha$ -methoxyalkyl hydroperoxides might decompose according to the reaction:



which should be much less favorable than reaction R5, but could affect our SCI yield measurements. The data also can be combined with SCI and aldehyde yields to evaluate the reaction mass balance.

The yields of  $C_{n-1}$  carboxylic acids are presented in Table 2. Yields ranged from a minimum of 0.010 for nonanoic acid to a maximum of 0.025 for tridecanoic acid, with no distinct trend and an average value of 0.019. The low acid yields observed here are consistent with values

measured for reactions of mostly smaller linear alkenes with  $O_3$  in the presence of high concentrations of SCI scavengers including water and methanol [20]. The yields are too small to significantly impact our SCI yield measurements, especially because the major pathway for carboxylic acid formation in the absence of water is thought to be through rearrangement of the excited CI [3]. Carboxylic acids also contribute little to the reaction mass balance. On the basis of our measured  $C_{n-1}$  SCI yields and the  $C_{n-1}$  carbonyl yields reported elsewhere [2,3], these two pathways appear to contribute  $\sim 60$ – $70\%$  of the product mass.

### 3.5. Analysis of $\alpha$ -hydroxyalkyl hydroperoxides formed from the gas-phase reaction of 1-octene with $O_3$ in the presence of water

The major SCI-scavenger in the ambient atmosphere is water vapor [9,21], which reacts to form  $\alpha$ -hydroxyalkyl hydroperoxides. These compounds appear to be relatively stable [17,22,23], but may undergo catalytic decomposition on surfaces or in solution. Because of the potential importance of these compounds, we conducted a chamber reaction with 1-octene and  $O_3$  under humid conditions to determine whether  $\alpha$ -hydroxyalkyl hydroperoxides could be analyzed via derivatization with MSTFA. Unfortunately, we were unable to detect any TMS  $\alpha$ -hydroxyalkyl hydroperoxide. This is probably due to the lower stability of  $\alpha$ -hydroxyalkyl hydroperoxides collected in solution, compared to  $\alpha$ -methoxyalkyl hydroperoxides. In support of this, we note that the post-reaction heptanal concentration (measured by GC-FID analysis of Tenax TA samples) for reaction under humid conditions was  $\sim 20\%$  higher than for reaction in the presence of methanol. The amount of heptanal formed by reaction R1b should be the same in both cases, so the excess measured in the humid reaction most likely comes from decomposition by reaction R4.

## 4. Conclusions

In this study, the use of off-line hydroperoxide derivatization by the trimethylsilylating reagent, MSTFA, was evaluated for quantitative analysis of thermally labile hydroperoxides using gas chromatography. Analysis of commercially available cumene hydroperoxide demonstrated that hydroperoxides can be derivatized with greater than 90% efficiency over a wide range of solution concentrations, and that this technique allows for quantitative analysis of these compounds. The technique was subsequently used to study the formation of  $\alpha$ -methoxyalkyl hydroperoxides formed from both solution and gas-phase ozonolysis of terminal alkenes ( $n = 8, 9, 10, 12,$  and  $14$ ) in the presence of methanol. Major products identified from this reaction were  $C_{n-1}$  aldehydes,  $C_{n-1}$  methyl esters, and  $C_{n-1}$   $\alpha$ -methoxyalkyl hydroperoxides. The yields of  $C_{n-1}$  stabilized Criegee intermediates (SCIs) from these

reactions were calculated as the sum of the  $C_{n-1}$  methyl ester and  $C_{n-1}$   $\alpha$ -methoxyalkyl hydroperoxide yields. The  $C_{n-1}$  SCI yields for the reactions of 1-octene, 1-nonene, and 2-methyl-1-octene were consistent with expectations based on literature data, whereas yields for reactions of 1-decene, 1-dodecene, and 1-tetradecene were much lower than expected. The discrepancy for the latter alkenes is attributed to side reactions of  $\alpha$ -methoxyalkyl hydroperoxides with aldehydes to form peroxyhemiacetals, which are not amenable to GC analysis. Attempts to prepare stable TMS  $\alpha$ -hydroxyalkyl hydroperoxides were unsuccessful, probably because of the greater tendency for these compounds to decompose.

Overall, the results of this study indicate that formation of TMS hydroperoxide derivatives, via MSTFA derivatization, can be an effective means for increasing the stability of otherwise thermally labile hydroperoxides for quantitative GC analysis. Although our analyses were performed on laboratory-generated samples, this method has the potential for use in analysis of environmental samples. Hydroperoxides can be formed in many different types of atmospheric reactions (including those initiated by OH radicals), and the role they might play in the observed deleterious effects of atmospheric aerosol particles on human health is currently of much interest.

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