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Article

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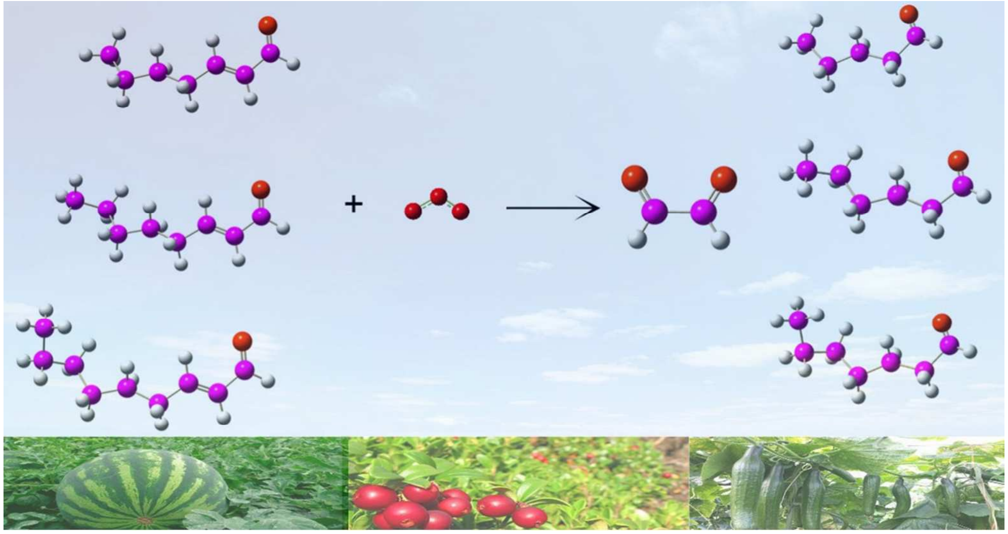

TOC

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Mechanism and Product Distribution of the O_3-Initiated Degradation of *(E)*-2-Heptenal, *(E)*-2-Octenal and *(E)*-2-Nonenal

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Abstract

The O_3-molecule initiated degradation of three 2-alkenals *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal has been investigated in a 1080 L quartz-glass environmental chamber at 298 ± 2 K and atmospheric pressure of synthetic air using *in situ* FTIR spectroscopy to monitor the reactants and products. The experiments were performed in the absence of OH scavenger. The molar yields of the primary products formed were glyoxal (49 ± 4) % and pentanal (34 ± 3) % from the reaction of *(E)*-2-heptenal with O_3, glyoxal (41 ± 3) % and hexanal (39 ± 3) % from the reaction of *(E)*-2-octenal with O_3 and glyoxal (45 ± 3) % and heptanal (46 ± 3) % from the reaction of *(E)*-2-nonenal with O_3. The residual bands in the infrared product spectra for each of the studied reactions are attributed to 2-oxoaldehyde compounds. Based on the observed products, a general mechanism for the ozonolysis reaction of long chain unsaturated aldehydes is proposed and the results are compared with the available literature data.

Introduction

The C7-C9 2-alkenals *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal are volatile organic compounds present in cranberries,[1,2] *Citrullus lanatus,*[3] and raw potatoes. [4] *(E)*-2-Nonenal has been detected as a volatile organic constituent of *Cucumis sativus L.*[5,6] and apples.[7] The emissions of these compounds are attributed to lipid oxidation in the vegetal membrane.[8-10] Biodiesels also emit aldehydes, Cahill and Okamoto[11] and do N. Batista et al.[12] have reported among other aldehydes the emission of 2-heptenal from the combustion of soybean- and animal-based biodiesel. Additionally, oils at frying temperatures emit several aldehydes among them *(E)*-2-alkenal type aldehydes with C3-C11 carbon chains and also toxic oxygenated *(E)*-2-alkenal type aldehydes.[13]

Unsaturated aldehydes once emitted to the atmosphere will be subject to degradation by photolysis and reaction with OH radicals during day and by reaction with NO_3 radicals during the late evening and night. Reaction of unsaturated aldehydes with O_3 molecules is possible both day and night but will only play a significant role in polluted areas with elevated ozone concentrations. Recent studies have shown that the gas-phase and aqueous-phase oxidation of these compounds can form secondary organic aerosols (SOA) and that they are precursors for polar organosulphates which have been found in ambient aerosol.[14-16]

We have previously reported a kinetic study on the reaction of O_3 with *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal at 298 K using the relative rate method, the obtained k_{O3} in units of $\times 10^{18}$ ($cm^3 molecule^{-1} s^{-1}$) were: (2.47 ±0.73) for *(E)*-2-heptenal, (2.37 ± 0.68) for *(E)*-2-octenal and (2.05 ± 0.20) for *(E)*-2-nonenal.[17] These rate coefficients showed that for the studied long-chain aldehydes increasing the alkyl chain length has a virtually negligible influence on the measured rate coefficients, i.e. above C3 the electron-donating effect of the alkyl chain has no further effect on the reactivity of the double bond toward O_3 addition. Kinetic studies for reaction of these aldehydes with other atmospheric oxidants have been reported. A room temperature rate coefficient for the reaction of OH radicals with *(E)*-2-heptenal has been reported by Albaladejo et al.[18] and Davis et al.[19] have investigated the temperature dependence of the reaction over the range 244 – 374 K. Gao et al.[20] have determined the rate coefficients for the reactions of OH radicals with *(E)*-2-octenal and *(E)*-2-nonenal at 298K. A room temperature rate coefficient for the reaction of *(E)*-2-heptenal with NO_3 radicals has been obtained by Zhao et al.[21] Kerdouci et al. [22] have reported a value for the same reaction at 204 K in addition to a rate coefficient for the reaction of *(E)*-2-octenal with NO_3 radicals. Finally, Rodríguez et al. [23] have measured the rate coefficient for the reaction of Cl atoms with *(E)*-2-heptenal at room temperature.

There have been a number of previous product studies on the reaction of O_3 with unsaturated aldehydes, most of them, however, on short-chain aldehydes ($<C_6$). Grosjean et al.[24] have studied the products resulting from the ozonolysis of the C3 2-alkenal acrolein ($CH_2=CHC(O)H$) at temperatures between 12-17°C, Grosjean and Grosjean[25] have investigated the products from the ozonolysis of the C4 2-alkenal crotonaldehyde ($CH_3CH=CHC(O)H$) at room temperature and Grosjean et al.[26] the products resulting from the reaction of O_3 with the C6 2-alkenal *trans*-2-hexenal at ambient temperature. More recently, Uchida et al.[27] have studied the products produced in the ozonolysis of the C6 3-alkenal *(Z)*-3-hexenal under atmospheric conditions. To our knowledge, there are no previous products studies for the reactions of OH radicals with the C7-C9 2-alkenals under study in this work, however, Kerdouci et al.[22] have reported product analyses for the reactions of NO_3 radicals with *(E)*-2-hexenal, *(E)*-2-heptenal and *(E)*-2-octenal where they

observed that unsaturated peroxynitrate type compounds were the main products formed via H-atom abstraction by NO_3 from the aldehyde entity and subsequent consecutive additions of O_2 and NO_2 to the resulting $CH_3(CH_2)_nCH=CHC(=O)$ radicals (n = 2, 3 or 4).

The primary aim of the present work is to identify and quantify the gas-phase products produced in the room temperature ozonolysis of the long-chain C7-C9 2-alkenals *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal. Identification of the primary reaction products generated in the ozonolysis of the 2-alkenals will provide information on the effect of the aldehyde functionality on the fragmentation of the primary ozonide compared to that observed for alkyl substituted alkenes. The secondary aim of the study is to postulate mechanisms for the reactions leading to the observed products and to evaluate potential atmospheric implications of the reactions. To the best of our knowledge, this work represents the first report of products and product yields for the ozonolysis of the long-chain aldehydes *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal.

Experimental set up

A 1080 L reaction chamber was used to perform the experiments at (298 ± 2) K in 750 Torr of synthetic air. The chamber consists of two cylindrical quartz glass vessels, each 3 m in length and 45 cm inner diameter, joined in the middle with both open ends closed by aluminium flanges. The reactants and the bath gases were introduced through ports located on the metal flanges. To ensure homogeneous mixing of the reactants three fans with Teflon blades are mounted inside the chamber. The reaction chamber can be evacuated to $<10^{-3}$ Torr by a pumping system consisting of a turbomolecular pump backed by a double stage rotary fore pump. White-type mirrors mounted internally in the chamber are coupled via an external optical transfer system to a Thermo Nicolet Nexus FTIR spectrometer. The "White" mirror system in the chamber was operated with the total optical absorption path length set to 484.7 m. The spectrometer is equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. This setup enables "*in situ*" monitoring of the reactants and products in the infrared range 4000-700 cm^{-1}. Infrared spectra were recorded with a spectral resolution of 1 cm^{-1}.

For the experiments of the ozonolysis of *(E)*-2-heptenal, 80 interferograms were co-added per spectrum and 20 such spectra were recorded per experiment, for the ozonolysis of *(E)*-2-octenal 75 interferograms were co-added per spectrum and 22 such spectra were recorded per experiment and for the ozonolysis of *(E)*-2-nonenal 100 interferograms were co-added per spectrum and 25 such spectra were recorded per experiment. The reactor is described in greater details in Barnes et al. [28,29]

Ozone was produced by flowing O_2 through an electrical discharge and was added continuously to the chamber containing the aldehyde homogeneously mixed in synthetic air. The O_3 concentration introduced into the chamber was up to a maximum of 7 ppmV. The experiments were performed in the absence of an OH radical scavenger since addition of very large concentrations of scavengers such as CO or cyclohexane would have been necessary to scavenge the OH in the reaction systems and such large concentrations would have made an FTIR analysis of the system impossible. The consequences of the non-use of an OH radical scavenger in the experiments for the results are discussed in detail further in the Results and Discussion section. Two experiments were performed for each of the studied reactions.

Reaction products were quantified by comparison with reference spectra contained in the IR spectral database of the laboratory in Wuppertal. Pentanal and hexanal were quantified using absorption cross sections from the database of the laboratory in Wuppertal while glyoxal and heptanal were quantified using cross section values reported by Volkamer et al.[30] and Beaver et al.,[31] respectively. All three unsaturated aldehydes were monitored in the infrared absorption region 2700-3000 cm^{-1}. Identified products were monitored at the following infrared absorption regions (in cm^{-1}): glyoxal, 2748-2910; pentanal, 2650-3000; hexanal, 2600-3000; heptanal, 2650-3000. The initial concentrations of the unsaturated aldehydes in ppm (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K) were *(E)*-2-heptenal 0.87-0.88; *(E)*-2-octenal 0.77-0.83 and *(E)*-2-nonenal 0.64-0.66.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), *(E)*-2-heptenal (Aldrich 97%), *(E)*-2-octenal (Aldrich, ≥95%) and *(E)*-2-nonenal (Aldrich, 97%)

Results and Discussion

Figure 1, panel A, shows the infrared spectrum of a *(E)*-2-heptenal/O_3/air gas mixture after reaction and subtraction of residual *(E)*-2-heptenal. Reference spectra of glyoxal and pentanal are shown in panels B and C, and panel D shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A. Similarly, Figure S1 (see Supplementary Information, SI), panel A, shows the infrared spectrum of a *(E)*-2-octenal/O_3/air gas mixture after reaction and subtraction of residual *(E)*-2-octenal (Panel A). Reference spectra of glyoxal and hexanal are shown in panels B and C, and panel D shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A. Figure S2 shows the same infrared spectral information obtained from experiments performed on a *(E)*-2-nonenal/O_3/air gas mixture, however, in this case panel C shows a reference spectrum of heptanal.

Formation of pentanal, hexanal and heptanal has been positively identified in the ozonolysis of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal, respectively. Glyoxal was identified as product in the ozonolysis of all three unsaturated aldehydes. Concentration−time profiles of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal and the identified products are presented in Figures 2, S3 and S4, respectively. Plots of the concentrations of the products as a function of consumed 2-alkenal are shown in Figures 3, S5 and S6 for *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal, respectively. Reasonably good linear correlations were observed in all cases. The molar product yields obtained from linear least-squares analyses of the plots in Figures 3, S5 and S6 are listed in Table 1. The errors given in Table 1 are the 2σ standard deviations from the analyses of the plots.

Ozonolysis reactions of unsaturated organics are initiated by addition of the O_3 molecule to the double bond of the compound to form a 1,2,3-trioxolane primary ozonide. This primary ozonide is energy rich and rapidly decomposes by cleavage of a C-C and an O-O bond to form a primary carbonyl and an initially vibrationally excited biradical known as a Criegee Intermediate (CI). The excited CI can unimolecular decompose ejecting an $O(^3P)$ atom, isomerize to form a hydroperoxide, rearrange to form an ester or acid or can be collisionally stabilized with the bath gas molecules.[32,33] The so-called hydroperoxide channel is known to form OH radicals to varying degrees through decomposition of the hydroperoxide.[34-36]

A very simplified general mechanism for the reaction of O_3 with *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal, not showing all possible reactions channels, is shown in Figure 4. The O_3 molecule reacts with the 2-alkenals by addition to the double bond to form a primary ozonide, which decomposes through channels A and B indicated in Figure 4. Decomposition of the ozonide through channel A forms glyoxal HC(O)C(O)H and $CH_3(CH_2)_nC{\cdot}HOO{\cdot}$ Criegee biradical where "n" indicates the number of $-CH_2-$ groups, i.e. 3, 4 and 5 for *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal, respectively. The vibrationally excited biradicals formed through channel A can potentially react via the hydroperoxide channel. Decomposition of the hydroperoxide can produce OH radicals and further reactions of the organic radical co-product can lead to the formation of a 2-oxoaldehyde and a hydroperoxide radical as shown in Figure 4. Due to the lack of reference spectra we are currently not able to unambiguously confirm whether or not the 2-oxoaldehyde formation channel is operative. The alkoxy radical ($CH_3(CH_2)_mCH(O{\cdot})CH(O)$) can also isomerize as it is shown in Figure 4. We proposed the 1,5 hydrogen shift of the alkoxy radical when m=2 (from the ozonolysis of *(E)*-2-heptenal). The isomerization and subsequence reaction with O_2 and peroxy radical can lead to other 1,5 hydrogen shift of the new alkoxy radical to finally formed a hydroxydicarbonyl compound through reaction with O_2. On the other hand, decomposition of the primary ozonide through channel B forms the $HC(O)C{\cdot}HOO{\cdot}$ Criegee biradical and the corresponding saturated aldehydes $CH_3(CH_2)_nC(O)H$ (n = 3, 4, or 5) which in the case of the ozonolysis of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal will be pentanal, hexanal and heptanal, respectively.

Under our experimental conditions the ozonolysis of *(E)*-2-heptenal forms glyoxal and pentanal as primary products with molar yields of (49 ± 4) % and (34 ± 3) %, respectively. In the case of *(E)*-2-octenal the primary products are glyoxal and hexanal with yields of (41 ± 3) % and (39 ± 3) %, respectively, and in the case of *(E)*-2-nonenal glyoxal and heptanal with yields of (45 ± 3) % and (46 ± 3) %, respectively. As mentioned previously in the Introduction section, the ozonolysis products of the three 2-alkenals studied here have not been previously reported in the literature; therefore, a direct comparison with other studies for the same 2-alkenals is not possible.

As already stated a number of times the ozonolysis of alkenes is known to produce OH radicals[36] which can influence the yields of the primary carbonyls measured in the ozonolysis of the 2-alkenals studied here. The OH radical yields for the ozonolysis of a large number of alkenes have been reported in the literature,[36] however, none have been reported to date for 2-alkenals under study. Rickard et al.[37] have developed a structure activity relationship (SAR) to rationalize the OH yields in ozone-alkene reactions as a function of the alkene structure, however, unfortunately this SAR can not be applied to estimate OH yields for 2-alkenals. The Criegee biradicals formed in the ozonolysis of the unsaturated aldehydes will have the structures $CH_3(CH_2)_nC{\cdot}HOO{\cdot}$ (n = 3, 4 or 5) and $HC(=O)C{\cdot}HOO{\cdot}$ and can potentially form the hydroperoxides $CH_3(CH_2)_nCH{=}CHOOH$ (n = 2, 3, 4) and O=C=CH-OOH, respectively. It is known from studies on the ozonolysis of alkenes that decomposition of $CH_3(CH_2)_nCH{=}CHOOH$ hydroperoxides will undoubtedly produce OH radicals to some degree,[36] however, nothing is currently known about the formation and fate of the O=C=CH-OOH hydroperoxide. If O=C=CH-OOH is formed, on decomposition it could form OH radicals and ethylenedione (O=C=C=O) and/or CO/CO_2:

$$O{=}C{=}CH\text{-}OOH \rightarrow (O{=}C{=}CH\text{-}O{\cdot} \leftrightarrow O{=}C({\cdot})\text{-}C({=}O)H) + {\cdot}OH$$

$$O{=}C{=}CH\text{-}O{\cdot} + O_2 \rightarrow O{=}C{=}C{=}O + HOO{\cdot}$$

$$O{=}C({\cdot})\text{-}C({=}O)H + O_2 \rightarrow\rightarrow CO + CO_2 + HOO{\cdot}$$

Ethylenedione has only recently been detected spectroscopically [38] and is known to be intrinsically short-lived and to dissociate to give two ground-state CO molecules. If formed, and long enough lived, it would absorb in the infrared region between the CO and CO_2 absorptions as is observed for carbon suboxide (O=C=C=C=O).[39] In the infrared region from 2000 to 2400 cm^{-1}, only absorptions due to CO and CO_2 are visible in the product spectra and there is nothing to indicate the intermediary formation of a compound such as ethylenedione. Also the amount of CO that was in the reaction system initially did not change during the course of the ozonolysis. Unfortunately, it is not possible to say what the trend is in CO_2 since the signal in the CO_2 absorption region is saturated due to CO_2 in the transfer optics housing between the chamber and FTIR spectrometer. However, the infrared and CO concentration observations support that the O=C=CH-OOH hydroperoxide channel and thus OH radical formation is probably not occurring for the HC(=O)C·HOO· Criegee biradical. Possible other reactions of the excited HC(=O)C·HOO· biradical include i) ejection of an O atom through *the O-atom channel* to form glyoxal, ii) isomerization via *the "hot" acid channel* with formation of glyoxylic acid (HC(=O)C(=O)OH) and iii) stabilization of the excited biradical. The product spectra of the three alkenals were compared with an IR spectrum of glyoxylic acid and we do not observed the formation of this acid (see Figure S7), therefore, we assumed that ejection of an O-atom to form glyoxal and collisional stabilization of the biradical are the main fates of the excited HC(=O)C·HOO· biradical. The stabilized HC(=O)C·HOO· biradical is also quite likely under our experimental conditions to react further to form glyoxal. This observation has consequences for the interpretation of the preferred fragmentation channel of the primary ozonide and is discussed further below. Additionally, Uchida et al.[27] in their study of the ozonolysis of *(Z)*-3-hexenal proposed that the alkyl chain biradical can decompose through two pathway. Based on their work, the alkyl substituted biradical of the ozonolysis reaction under study $CH_3(CH_2)_nC{\cdot}HOO{\cdot}$ (n = 3, 4 or 5) can undergo the following decomposition pathway:

$$CH_3(CH_2)_nC{\cdot}HOO{\cdot}\ (n = 3, 4 \text{ or } 5) \rightarrow CO + OH + CH_3(CH_2)_n$$

$$CH_3(CH_2)_nC{\cdot}HOO{\cdot}\ (n = 3, 4 \text{ or } 5) \rightarrow CO_2 + CH_3(CH_2)_xCH_3\ (x= 2, 3 \text{ or } 4)$$

However, as stated above, we did not observe variations in the CO or CO_2 concentrations in our experimental conditions. For the second reaction, where an alkane is formed, we compare the *n*-butane, *n*-pentane and *n*-hexane infrared spectra with the residual product spectra of the ozonolysis of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal, respectively. The C-H stretching region from $-CH_2-$ and $-CH_3$ groups (2800-3032 cm^{-1}) of the alkanes was no observed in the residual product spectra of the studied reactions.

Paulson et al.[40] have determined an OH yield of 16 % for the ozonolysis of methyl vinyl ketone ($CH_2=CHC(=O)CH_3$) and Uchida et al.[27] have reported an OH formation yields of 32 % for the ozonolysis of (*Z*)-3-hexenal ($CH_3CH_2CH=CHCH_2C(O)H$). Since in our ozonolysis systems it would appear, based on the discussion above, that only the $CH_3(CH_2)_nC{\cdot}HOO{\cdot}$ (n = 3, 4 or 5) Criegee biradicals will be producing OH, based on the work of Uchida et al.[27] we estimate that OH radical production is probably of the order of 15 % or less.

Despite the possible effect that OH radical reactions can have on the yields of the primary carbonyls measured for the ozonolysis of the C7-C9 2-alkenals, the measured yields are very similar to those reported in the literature for shorter chain 2-alkenals. Grosjean et al.[26] have studied the product formation from the ozonolysis of the C6 2-alkenal *trans*-2-hexenal and obtained formation yields for the primary products glyoxal and butanal of (55.9 ± 3.7) % and (52.7 ± 5.5) %, respectively. The experiments were carried out in a Teflon chamber at 298K and 760 Torr monitoring the O_3 concentration by ultraviolet photometry and analyzing the carbonyl compounds by liquid chromatography with UV detection. In the experiments cyclohexane was added to scavenge any OH radicals formed. Uchida et al.[27] have studied the product formation from the ozonolysis of the C6 3-alkenal *(Z)*-3-hexenal in a chamber at 298 K and 1 atm using in-situ long-path Fourier transform infrared (FTIR) spectroscopy for the analysis. The authors report a yield of (35 ± 1) % for the primary product propanal obtained using 1,3,5-trimethylbenzene and CO as OH radical scavengers.

Grosjean and Grosjean [24] have studied the products formed in the ozonolysis of the C3 2-alkenal acrolein ($CH_2=CHCHO$) and Grosjean and Grosjean[25] those formed in the ozonolysis of the C4 alkenal crotonaldehyde ($CH_3CH=CHCHO$). The experiments of Grosjean and Grosjean[24] on the ozonolysis of acrolein were performed at 17, 14, 13 and 12°C in a 3.5 m^3 Teflon chamber, cyclohexane was used as an OH radical scavenger and the carbonyl products were sampled on cartridges coated with 2,4-dinitrophenyhydrazine and subsequently analyzed by liquid chromatography with ultraviolet detection. The main carbonyl compounds detected were formaldehyde and glyoxal. The authors give amount of the carbonyls formed in ppb, however, unfortunately they do not provide any yield information. The experiments of Grosjean and Grosjean[25] on the ozonolysis of crotonaldehyde were similarly performed in a large volume FEP Teflon chamber at ambient temperature and atmospheric pressure in the presence of cyclohexane as an OH radical scavenger. The O_3 concentration was monitored by ultraviolet photometry and the concentration of the carbonyl compounds were analyzed by liquid chromatography with UV detection after collection on cartridges. In this study the authors report formation yields of the primary carbonyl products glyoxal and acetaldehyde of (47 ± 2) % and (42 ± 3) %, respectively.

Based on the generally accepted mechanism for the ozonolysis of alkenes the sum of the yields of the two primary carbonyl products formed from the two possible primary ozonide decomposition channel (see Figure 4) should be unity. The sum of the primary carbonyls is (83 ± 7) % for the ozonolysis of *(E)*-2-heptenal, (80 ± 6) % for the ozonolysis of *(E)*-2-octenal, (91 ± 6) % for the ozonolysis of *(E)*-2-nonenal. The sums of the yields of the primary carbonyls from the ozonolysis of the *(E)*-2-alkenals studied here is ≥ 80% and there is no apparent preference for one of the two decomposition routes of the primary ozonide with only a slight basis in the case of (*E*)-2-heptenal for the glyoxal forming channel. However, it should be noted that the sum of the yields of two primary carbonyl products (glyoxal and alkanal) could be higher than unity due to glyoxal yield include the oxygen ejection pathway contribution. As can be deduced from the above discussion on other literature studies on the ozonolysis of 2-alkenals similar yields and no trend toward a particular primary ozonide decomposition channel have also been observed in these studies.

It is interesting to note that the biradicals formed from the decomposition of the primary ozonide through channels A and B (see Figure 4) are both mono-substituted biradicals, the only difference being the type of the substituent. The biradical formed through channel A has an alkyl chain substituent and the biradical formed through channel B has an acyl group substituent. Studies have shown that the ozonolysis of asymmetrically alkyl-substituted alkenes generally results in preferential formation of the more substituted biradical.[41,42] Moreover, Wegener et al.[43] state that after decomposition of the primary ozonide generally electron-donating substituents remain in the biradical while electron acceptor substituents will be found in the carbonyl compound. However, as discussed above such a preference has not observed for the 2-alkenals studied here and also for the other 2-alkenals reported in the literature all of which contain an electron-acceptor, acyl, and an electron-donating, alkyl, substituent. There is conjugation between the carbonyl group and the double bond in the 2-alkenals and we speculate that the addition of ozone may not form a primary ozonide in the classical sense as is accepted for alkyl substituted alkenes and that the preferential fragmentation patterns observed for alkyl substituted alkenes may not apply for 2-alkenals and possibly also 2-alkenones.

After subtraction of the infrared adsorptions due to the identified compounds for each of the studied reactions, the residual infrared spectra (see panel D in Figures 1, S2, and S3) show distinct absorption bands in the carbonyl-stretching region (~1757 cm^{-1}) and the C-H stretching region from $-CH_2$ and $-CH_3$ groups (2880-3000 cm^{-1}). As noted previously, 2-oxoaldehyde compounds are potential reaction products, formation of which can not be experimentally validated due to the lack of authentic samples of the compounds. Grosjean et al.[26] have observed the formation of 2-

oxobutanal with a yield of ~7.4 % in the ozonolysis *(E)*-2-hexenal, therefore, formation of 2-oxoaldehydes in our study on the ozonolysis of C7-C9 2-alkenals is expected to be likely. In order to try and verify formation of 2-oxoaldehydes in the ozonolysis reactions infrared spectra have been computed for 2-oxopentanal (proposed product from the reaction of *(E)*-2-heptenal + O_3), for 2-oxohexanal (proposed product from the reaction of *(E)*-2-octenal + O_3) and for 2-oxoheptanal (proposed product from the reaction of *(E)*-2-nonenal + O_3). The computed spectra were obtained with the Gaussian 09 package at the B3LYP/6-311++G (d, 2p) level of theory.[44-46] Figure 5 shows a comparison between the computed IR spectrum for the expected product 2-oxopentanal and the residual experimental product IR spectrum obtained from the ozonolysis *(E)*-2-heptenal after subtraction of the primary carbonyl products. Figures S8 and S9 show the corresponding comparisons for the ozonolysis of *(E)*-2-octenal and *(E)*-2-nonenal where 2-oxohexanal and 2-oxoheptanal, respectively, are the potential 2-oxoaldehyde products. The salient features from the residual spectra for each of the studied reactions show similarity with the computed spectra. This similarity suggests that many of the absorption features in the residual product spectra obtained from the ozonolysis of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal are quite possibly due to the formation of 2-oxopentanal, 2-oxohexanal and 2-oxoheptanal, respectively. However, an infrared spectrum of each of the oxoaldehyde compounds obtained from an authentic sample of the compound is necessary for an absolute validation of their formation. The residual spectra may also contain absorptions from other carbonyl compounds, such as the hydroxydicarbonyl compounds from the isomerization of the alkoxy radical that have been previously mentioned, however, in Figures 1, S1 and S2 there are not observed the infrared band corresponding to the stretching of OH group (3500-3600cm-1), other possibility is the formation of epoxy compounds, even though the epoxy pathway in gas phase ozonolysis reactions is considered to be a minor pathway.[47-48]

In summary, the ozonolysis of the C7-C9 *(E)*-2-alkenal compounds studied in this work leads to the formation as primary products the dicarbonyl compound glyoxal and the corresponding saturated aldehydes pentanal, hexanal and heptanal. The yields of the primary carbonyl products were all quite similar with combined total carbonyl yields of ≥ 80% for each of the studied reactions. No preference was found for the two possible primary ozonide decomposition in agreement with other studies on shorter chain 2-alkenals and contrary to what one would expect based ozonolysis studies of alkyl substituted alkenes.

Atmospheric implications

In a previous work, we have reported the atmospheric lifetimes of the studied 2-alkenals using the typical ambient concentrations for the tropospheric oxidants (OH, O_3, Cl). The calculated lifetimes indicated that the reaction with OH and NO_3 (few hours) radicals are the main degradation processes for these aldehydes in the atmosphere, reaction with O_3 possibly being of some importance in regions with high levels of O_3.[17] The ozonolysis reactions of these unsaturated aldehydes have been in this study and some other studies to be sources for alkyl aldehydes, dialdehydes and possibly other oxygenated compounds. Glyoxal can be degraded in the atmosphere by reaction with OH radicals[49] and via photolysis.[50] Fu et al.[51] have estimated the global production budget of glyoxal to be ~45 Tg/annum, even though, isoprene oxidation contributes to 47% of this globally glyoxal budget. Moreover, glyoxal plays an important role in global SOA formation via irreversible uptake by aqueous aerosols and clouds,[51-55] for example, De Haan et al.[55] have estimated that glyoxal can produce 1 Tg C/year SOA due to self-reactions in a evaporating droplets. Additionally, it can be removed from the atmosphere through wet deposition due to its high water solubility.[56]

The alkyl aldehydes products of the studied reactions also have as main degradation processes in the atmosphere the reaction with OH radicals and photolysis. For example, pentanal has a lifetime of 5.1 h due to the reaction with OH radical (calculated using a noon time value of $[OH] = 2 \times 10^6$ molecule cm^{-3}) and a lifetime due to photolysis of 17 h.[57] The lifetime of hexanal due to the reaction with OH radicals has been estimated by Jiménez et al.[58] to be 10 h using a 24 h average of $[OH]= 1\times10^6$ molecule cm^{-3} at 298 K, which reduces to 4.9 h if $[OH]= 2\times10^6$ molecule cm^{-3} is used in the lifetime calculation. The lifetime of this aldehyde due to photolysis has been estimated to be < 48 h by Jiménez et al.[58] Finally, heptanal has an estimated lifetime of 4.7 h due to reaction with OH when calculated using a noon time value of $[OH]= 2\times10^6$ molecule cm^{-3} and $k_{OH}= 2.96\times10^{-11}$ $molecule^{-1}$ cm^{-3} s^{-1} [18] and a photolysis lifetime of 17 h, obtained using the photolysis rate of $(1.65 \pm 0.03)\times10^{-5}$ s^{-1} from Paulson et al.[59] These C5-C7 alkyl aldehydes have been detected in urban, rural and forest environments.[60-63] The atmospheric degradation of pentanal, hexanal, heptanal and glyoxal can produce free radical species that can contribute to O_3 formation and in the presence of NO_x could form organic nitrates or peroxynitrates which transport NO_x species to remote environments.

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References

(1) Anjou, K.; von Sydow, E. The Aroma of Cranberries I. Vaccinium vitis-idaea L. *Acta Chem. Scand.* **1967**, 21, 945-952.

(2) Zhu, J. C.; Chen, F.; Wang, L. Y.; Niu, Y. W.; Chen, H. X.; Wang, H. L.; Xiao, Z. B. Characterization of the Key Aroma Volatile Compounds in Cranberry (Vaccinium macrocarpon Ait.) Using Gas Chromatography−Olfactometry (GC-O) and Odor Activity Value (OAV). *J. Agric. Food Chem*. **2016**, 64, 4990− 4999.

(3) Beaulieu, J. C.; Lea, J. M. Characterization and Semiquantitative Analysis of Volatiles in Seedless Watermelon Varieties Using Solid-Phase Microextraction. *J. Agric. Food Chem*. **2006**, 54, 7789−7793

(4) Petersen, M. A.; Poll, L.; Larsen, L. M. Comparison of Volatiles in Raw and Boiled Potatoes Using a Mild Extraction Technique Combined with GC Odour Profiling and GC-MS. *Food Che.* **1998**, 61, 4,461-466.

(5) Palma-Harris, C.; McFeeters, R. F.; Fleming, H. Solid-Phase Microextraction (SPME) Technique for Measurement of Generation of Fresh Cucumber Flavor Compounds. *J. Agric. Food Chem.* **2001**, 49, 4203−4207.

(6) Atiama-Nurbel, T.; Quilici, S.; Boyer, E., Deguine, J.-P.; Glenac, S.; Bialecki, A. Volatile Constituents of *Cucumis sativus*: Differences Between Five Tropical Cultivars. *Chem. Nat. Compd.* **2015**, 51, 4, 771-775

(7) Fuhrmann, E.; Grosch, W. Character Impact Odorants of the Apple Cultivars Elstar and Cox Orange. *Nahrung/Food*. **2002**, 46, 3, 187-193.

(8) Zhou, A.; McFeeters, R. F.; Fleming, H. P. Development of Oxidized Odor and Volatile Aldehydes in Fermented Cucumber Tissue Exposed to Oxygen. *J. Agric. Food Chem*. **2000**, 48, 193−197.

(9) Xu, Y.; Barringer, S. E. Effect of Temperature on Lipid-Related Volatile Production in Tomato Puree. *J. Agric. Food Chem*. **2009**. 57, 9108–9113.

(10) Zhu, X.; Tang, X.; Anderson, V. E.; Sayre, L. M. Mass Spectrometric Characterization of Protein Modification by the Products of Nonenzymatic Oxidation of Linoleic Acid. *Chem. Res. Toxicol*. **2009**, 22, 1386–1397.

(11) Cahill, T. M.; Okamoto, R. Emissions of Acrolein and Other Aldehydes from Biodiesel-Fueled Heavy-Duty Vehicles. *Environ. Sci. Technol.* **2012**, 46, 8382− 8388.

(12) do N. Batista, L.; Da Silva, V. F.; Pissurno, E. C. G.; da Conceicao Soares, T.; de Jesus, M. R.; Kunigami, C. N.; Brasil, M. G.; da Fonseca, M. G. Formation of Toxic Hexanal, 2-Heptenal and 2,4-Decadienal During Biodiesel Storage and Oxidation. *Environ. Chem. Lett.* **2015**, 13, 353–358

(13) Guillén, M. D.; Uriarte,P. S. Aldehydes Contained in Edible Oils of a Very Different Nature After Prolonged Heating at Frying Temperature: Presence of Toxic Oxygenated

α, β- Unsaturated Aldehydes. *Food Chem*. **2012**, 131, 915–926.

(14) Shalamzari, M. S.; Kahnt, A.; Vermeylen, R.; Kleindienst, T. E.; Lewandowski, M.; Cuyckens, F.; Maenhaut, W.; Claeys, M. Characterization of Polar Organosulfates in Secondary Organic Aerosol from the Green Leaf Volatile 3-Z-Hexenal. *Environ. Sci. Technol*. **2014**, 48, 12671-12678.

(15) Shalamzari, M. S.; Vermeylen, R.; Blockhuys, F.; Kleindienst, T. E.; Lewandowski, M.; Szmigielski, R.; Rudzinski, K.J.; Spólnik, G.; Danikiewicz, W.; Maenhaut, W.; Claeys, M. Characterization of Polar Organosulfates in Secondary Organic Aerosol from the Unsaturated Aldehydes 2-E-Pentenal, 2-E-Hexenal, and 3-Z-Hexenal. *Atmos. Chem. Phys*. **2016**, 16, 7135-7148.

(16) Richards-Henderson, N. K.; Hansel, A. k.; Valsaraj, K. T.; Anastasio, C. Aqueous Oxidation of Green Leaf Volatiles by Hydroxyl Radical as a Source of SOA: Kinetics and SOA Yields. *Atmos. Environ*. **2014**, 95, 105-112.

(17) Gaona Colmán, E.; Blanco, M. B.; Barnes, I.; Teruel, M. A. Ozonolysis of a Series of C7–C9 Unsaturated Biogenic Aldehydes: Reactivity Study at Atmospheric Pressure. *RSC Adv*. **2015**, 5, 30500-30506.

(18) Albaladejo, J.; Ballesteros, B.; Jiménez, E.; Martín, P.; Martínez, E. A PLP–LIF Kinetic Study of the Atmospheric Reactivity of a Series of C4–C7 Saturated and Unsaturated Aliphatic Aldehydes with OH. *Atmos. Environ*. **2002**, 36, 3231-3239.

(19) Davis, M. E.; Gilles, M. K.; Ravishankara, A. R.; Burkholder, J. B. Rate Coefficients for the Reaction of OH with (E)-2-Pentenal, (E)-2-Hexenal, and (E)-2-Heptenal. *Phys. Chem. Chem. Phys*. **2007**, 9 2240 – 2248.

(20) Gao, T.; Andino, J. M.; Rivera, C. C.; Márquez, M. F. Rate Constants of the Gas-Phase Reactions of OH Radicals with trans-2-Hexenal, trans-2-Octenal, and trans-2-Nonenal. *Int. J. Chem. Kinet*. **2009**, 41, 483–489.

(21) Zhao, Z.; Husainy, S.; Smith, G. D. Kinetics Studies of the Gas-Phase Reactions of NO_3 Radicals with Series of 1-Alkenes, Dienes, Cycloalkenes, Alkenols, and Alkenals. *J. Phys. Chem. A.* **2011,** 115, 44, 12161–12172.

(22) Kerdouci, J.; Picquet-Varrault, B.; Durand-Jolibois, R.;Gaimoz, C.; Doussin, J. F. An Experimental Study of the Gas-Phase Reactions of NO_3 Radicals with a Series of Unsaturated Aldehydes: trans-2-Hexenal, trans-2-Heptenal, and trans-2-Octenal. *J. Phys. Chem. A*. **2012**, 116, 41, 10135-10142.

(23) Rodríguez, D.; Rodríguez, A.; Notario, A.; Aranda, A.; Díaz-de-Mera, Y.; Martínez, E. Kinetic Study of the Gas-Phase Reaction of Atomic Chlorine with a Series of Aldehydes. *Atmos. Chem. Phys.* **2005**, 5, 3433-3440.

(24) Grosjean, E.; Williams II, E. L.; Grosjean, D. Atmospheric Chemistry of Acrolein. *Sci. Total Environ.* **1994**, 153, 195-202.

(25) Grosjean, E.; Grosjean, D. The Gas Phase Reaction of Unsaturated Oxygenates with Ozone: Carbonyl Products and Comparison with the Alkene-Ozone Reaction. *J. Atmos. Chem.* **1997**, 27, 271–289.

(26) Grosjean, E.; Grosjean, D.; Seinfeld, J. H. Gas-Phase Reaction of Ozone with *trans*-2-Hexenal, *trans*-2-Hexenyl Acetate, Ethylvinyl Ketone, and 6-Methyl-5-hepten-2-one. *Int. J. Chem. Kinet.* **1996**, 28, 373-382.

(27) Uchida, R.; Sato, K.; Imamura, T. Gas-Phase Ozone Reactions with Z-3-Hexenal and Z-3-Hexenol: Formation Yields of OH Radical, Propanal, and Ethane. *Chem. Lett*. **2015**, 44, 457-458.

(28) Barnes, I; Becker, K. H.; Zhou, T. Near UV Absorption Spectra and Photolysis Products of Difunctional Organic Nitrates. *J. Atmos. Chem*. **1993**, *17*. 353-373.

(29) Barnes, I.; Becker, K. H.; Mihalopoulos, N. An FTIR Product Study of the Photooxidation of Dimehtyl Disulfide. *J. Atmos. Chem*. **1994**, *18*. 267-289.

(30) Volkamer R; Spietz P; Burrows J.; Platt U. High-Resolution Absorption Cross-Section of

Glyoxal in the UV/Vis and IR Spectral Ranges. *J. Photochem. Photobiol. A Chem*. **2005**, 172, 35-46.

(31) Beaver, M. R.; Elrod, M. J.; Garland, R. M.; Tolbert, M. A. Ice Nucleation in Sulfuric Acid/Organic Aerosols: Implications for Cirrus Cloud Formation. *Atmos. Chem. Phys*. **2006**, 6, 3231–3242

(32) Atkinson, R.; Carter, W.P.L. Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions. *Chem. Rev.* **1984**, 84, 437-470.

(33) Horie, O.; Moortgat, G. K. Gas-Phase Ozonolysis of Alkenes. Recent Advances in Mechanistic Investigations. *Acc. Chem. Res*. **1998**, 31, 387-396.

(34) Atkinson, R. Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes. *J. Phys. Chem. Ref. Data.* **1997**, *26*, 215-290.

(35) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, Moorgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Alkenes.* Oxford University Press, Oxford. **2000**.

(36) Calvert, J. G.; Orlando, J. J.; Stockwell, W. R.; Wallington, T. J. *The Mechanisms of Reactions Influencing Atmospheric Ozone*. Oxford University Press, Oxford. **2015**.

(37) Rickard, A. R.; Johnson, D.; McGill, C. D.; Marston, G. OH Yields in the Gas-Phase Reactions of Ozone with Alkenes. *J. Phys. Chem. A* 1999, *103,* 7656-7664.

(38) Dixon, A. R.; Xue, T.; Sanov, A. Spectroscopy of Ethylenedione. *Angew. Int. Ed*. **2015**, 54, 8764-8767.

(39) Miller, F. A.; Fateley, W. G. The Infrared Spectrum of Carbon Suboxide. *Spectrochim. Acta*. 1964, 20, 253-266.

(40) Paulson, S. E.; Chung, M.; Sen, A. D.; Orzechowska, G. Measurement of OH Radical Formation from the Reaction of Ozone with Several Biogenic Alkenes. *J. Geophys. Res*. **1998**, 103, D19, 25,533-25,539.

(41) Grosjean, E.; Grosjean, D. Carbonyl Products of the Gas-Phase Reaction of Ozone with 1-Alkenes. *Atmos. Environ.* **1996**, 30, 24, 4107-4113.

(42) Tuazon, E. C.; Aschmann, S. M.; Arey, J.; Atkinson, R. Products of the Gas-Phase Reactions Of O_3 with a Series of Methyl-Substituted Ethenes. *Environ. Sci. Technol*. **1997**, 31, 3004-3009.

(43) Wegener, R.; Brauers, T.; Koppmann, R.; Rodríguez Bares, S.; Rohrer, F.; Tillmann, R.; Wahner, A.; Hansel, A.; Wisthaler, A. Simulation Chamber Investigation of the Reactions of Ozone with Short-Chained Alkenes. *J. Geophys. Res*. **2007**, 112, D13301.

(44) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, 98, 5648 − 5652.

(45) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B*. **1988**, 37, 785 − 789.

(46) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett*. **1989**, 157, 200 −206.

(47) Atkinson, R. and Arey, J. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos. Environ*. **2003**, 37, S197-S219.

(48) Kramp, F. and Paulson, S. E. The gas phase reaction of ozone with 1,3-butadiene: formation yields of some toxic products. *Atmos. Environ*. **2000**, 34, 35-43.

(49) Plum, C. N.; Sanhuenza, E.; Atkinson, R.; Carter, W. P. L.; Pitts, J. N. Jr. OH Radical Rate Constants and Photolysis Rates of α-Dicarbonyls. *Environ. Sci. Technol*. **1983**, 17, 479-484.

(50) Tadić, J.; Moortgat, G. K.; Wirtz, K. Photolysis of Glyoxal in Air. *J. Photochem. Photobiol., A.* **2006**, 177, 116-124.

(51) Fu, T. M.; Jacob, D. J.; Wittrock, F.; Burrows, J. P.; Vrekoussis, M.; Henze, D. K. Global Budgets of Atmospheric Glyoxal and Methylglyoxal, and Implications for Formation of Secondary Organic Aerosols. *J. Geophys. Res*. **2008**, 113, D15303.

(52) Hastings, W. P.; Koehler, C. A.; Bailey, E. L.; De Haan, D. O. Secondary Organic Aerosol Formation by Glyoxal Hydration and Oligomer Formation: Humidity Effects and Equilibrium Shifts During Analysis. *Environ. Sci. Technol.* **2005**, 39, 8728–873.

(53) Liggio, J.; Li, S. M.; McLaren, R. Reactive Uptake of Glyoxal by Particulate Matter. *J. Geophys. Res.* **2005**, 110, D10304.

(54) Schaefer, T.; van Pinxteren, D.; Herrmann, H. Multiphase Chemistry of Glyoxal: Revised Kinetics of the Alkyl Radical Reaction with Molecular Oxygen and the Reaction of Glyoxal with OH, NO_3, and SO_4^- in Aqueous Solution. *Environ. Sci. Technol*. **2015**, 49, 343-350.

(55) De Haan, D. O.; Corrigan, A. L.; Tolbert, M. A.; Jimenez, J. L.; Wood, S. E.; Turley, J. J. Secondary Organic Aerosol Formation by Self-Reactions of Methylglyoxal and Glyoxal in Evaporating Droplets. *Environ. Sci. Technol*. **2009**, 43, 8184–8190.

(56) Matsunaga, S. N.; Guenther, A.; Izawa, Y.; Wiedinmyer, C.; Greenberg, J.; Kawamura, K. Importance of Wet Precipitation as a Removal and Transport Process for Atmospheric Water Soluble Carbonyls. *Atmos. Environ*. **2007**, 41, 790-796.

(57) Tadić, J.; Juranić, I.; Moortgat, G. K. Pressure Dependence of Photooxidation of Selected Carbonyl Compounds in Air: n-Butanal and n-Pentanal. *J. Photochem. Photobiol., A.* **2001**, 143, 169-179.

(58) Jiménez, E.; Lanza, B.; Martínez, E.; Albaladejo, J. Daytime Tropospheric Loss of Hexanal and trans-2-Hexenal: OH Kinetics and UV Photolysis. *Atmos. Chem. Phys*. **2007**, 7, 1565–1574.

(59) Paulson, S. E.; Liu, D. L.; Orzechowska, G. E. Photolysis of Heptanal. *J. Org. Chem*. **2006**, 71, 6403 -6408.

(60) Ciccioli, P.; Brabcaleoni, E.; Frattoni, M.; Cecinato, A.; Brachetti, A. Ubiquitous Occurrence of Semi-Volatile Carbonyl Compounds in Tropospheric Samples and their Possible Sources. *Atmos. Environ.* **1993**, 27A, 12, 1891-1901

(61) Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R. Air Quality Model Evaluation Data for Organics. 2. C1-C14 Carbonyls in Los Angeles Air. *Environ. Sci. Technol*. **1996**, 30, 2687-2703

(62) Hurst Bowman, J.; Barket, Jr. D.; Shepson, P. B. Atmospheric Chemistry of Nonanal. *Environ. Sci. Technol.* **2003**, 37, 2218-2225

(63) Guo, S.; Chen, M.; Tan, J. Seasonal and Diurnal Characteristics of Atmospheric Carbonyls in Nanning, China. *Atmos. Res.* **2016**, 169, 46–53

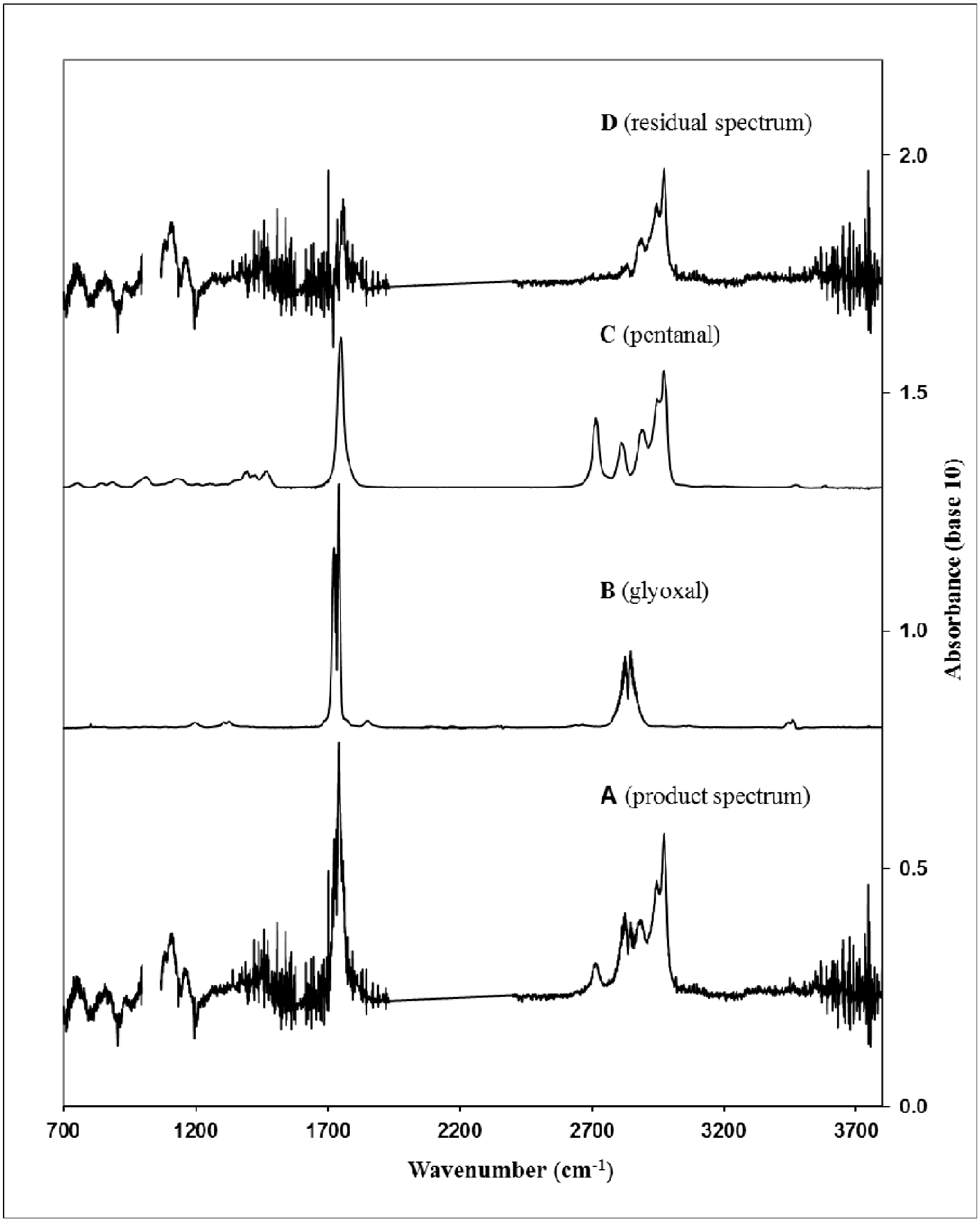

Figure 1: Panel A shows the infrared spectrum of a *(E)*-2-heptenal/O_3/air gas mixture after reaction and subtraction of residual *(E)*-2-heptenal. Panels B and C show reference spectra of glyoxal and pentanal, respectively. Panel D shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A. (A straight line is presented between 1900-2400 cm^{-1} for the spectra in panel A and D avoiding the CO_2 and CO absorption)

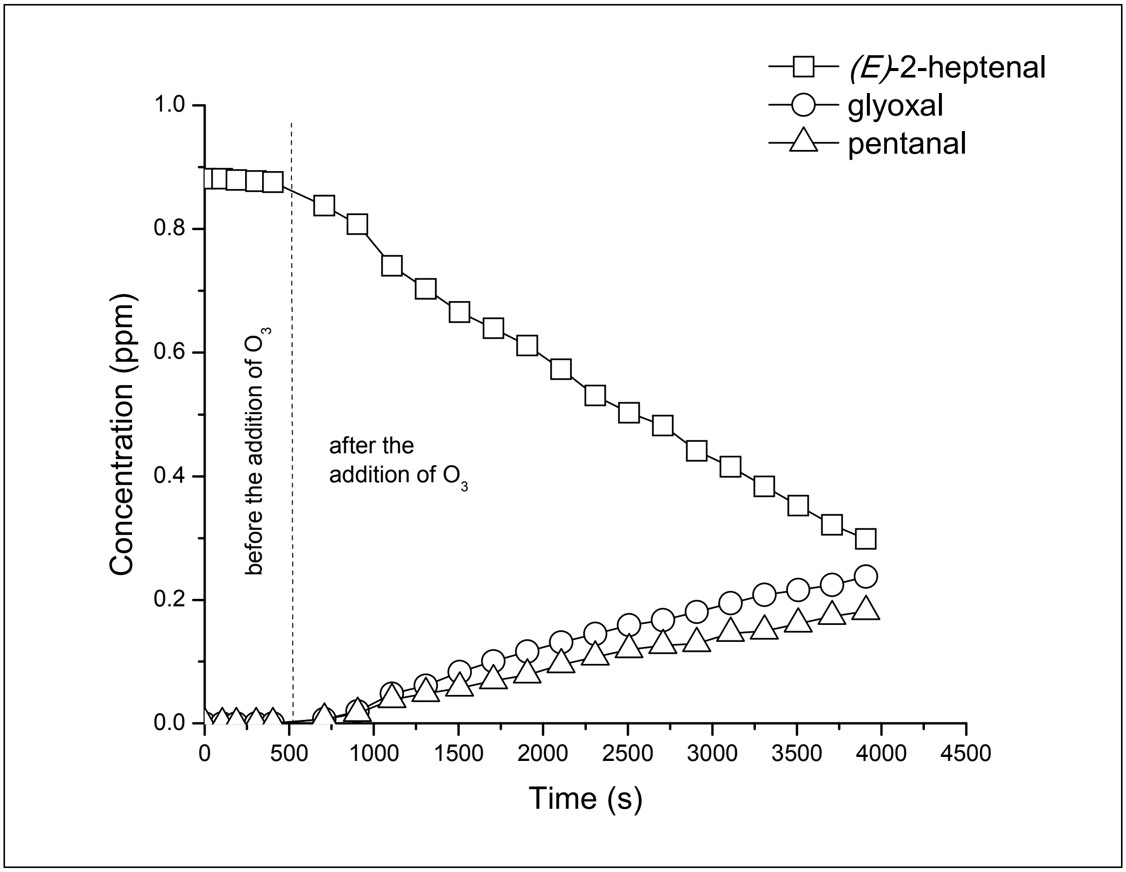

Figure 2: Concentration-time profiles of *(E)*-2-heptenal and the reaction products glyoxal and pentanal obtained from a *(E)*-2-heptenal /O_3/air reaction mixture.

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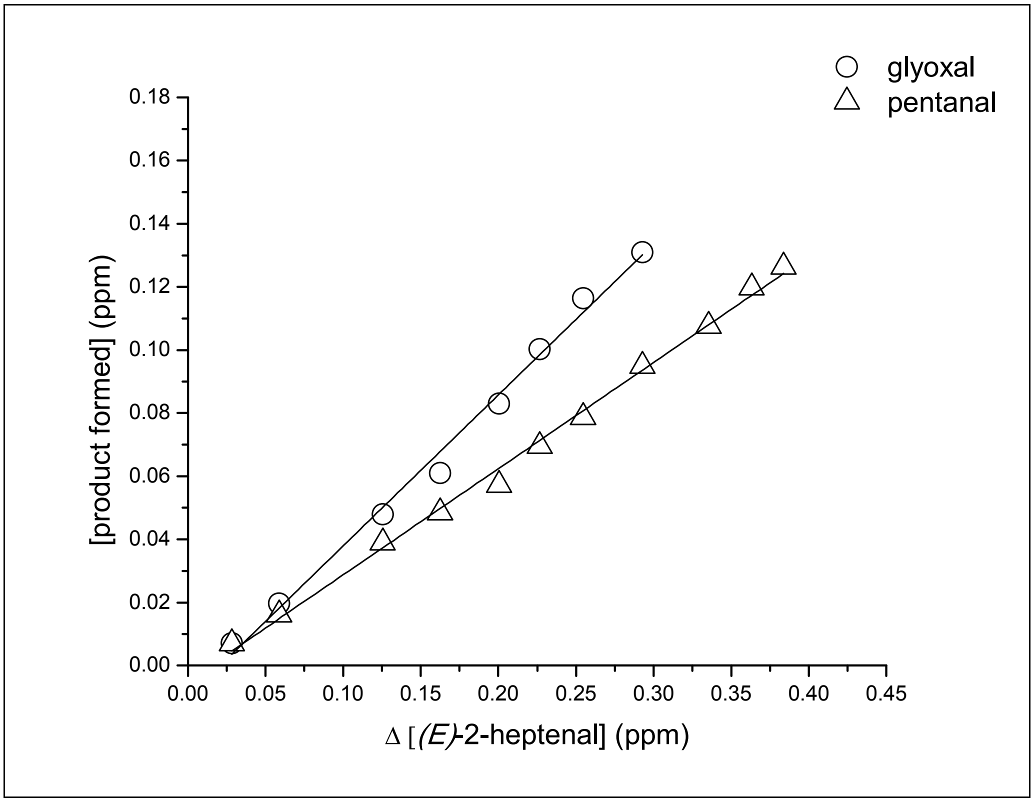

Figure 3: Plots of the concentrations of the reaction products glyoxal and pentanal as a function of reacted *(E)*-2-heptenal obtained from experiments performed on *(E)*-2-heptenal /O_3/air reaction mixtures.

Table 1

Formation yields of the oxidation products identified in the ozonolysis of *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal at 298K in 750 ± 10 Torr of air.

Compound	**Product**	**Yield (%)**
(E)-2-heptenal	$HC(O)C(O)H$	50 ± 4
	Glyoxal	48 ± 4
		average: 49 ± 4
	$CH_3(CH_2)_3C(O)H$	
	Pentanal	35 ± 3
		33 ± 2
		average: 34 ± 3
(E)-2-octenal	$HC(O)C(O)H$	41 ± 3
	Glyoxal	41 ± 3
		average: 41 ± 3
	$CH_3(CH_2)_4C(O)H$	
	Hexanal	38 ± 2
		39 ± 3
		average: 39 ± 3
(E)-2-nonenal	$HC(O)C(O)H$	45 ± 3
	Glyoxal	44 ± 3
		average: 45 ± 3
	$CH_3(CH_2)_5C(O)H$	
	Heptanal	47 ± 2
		45 ± 3
		average: 46 ± 3

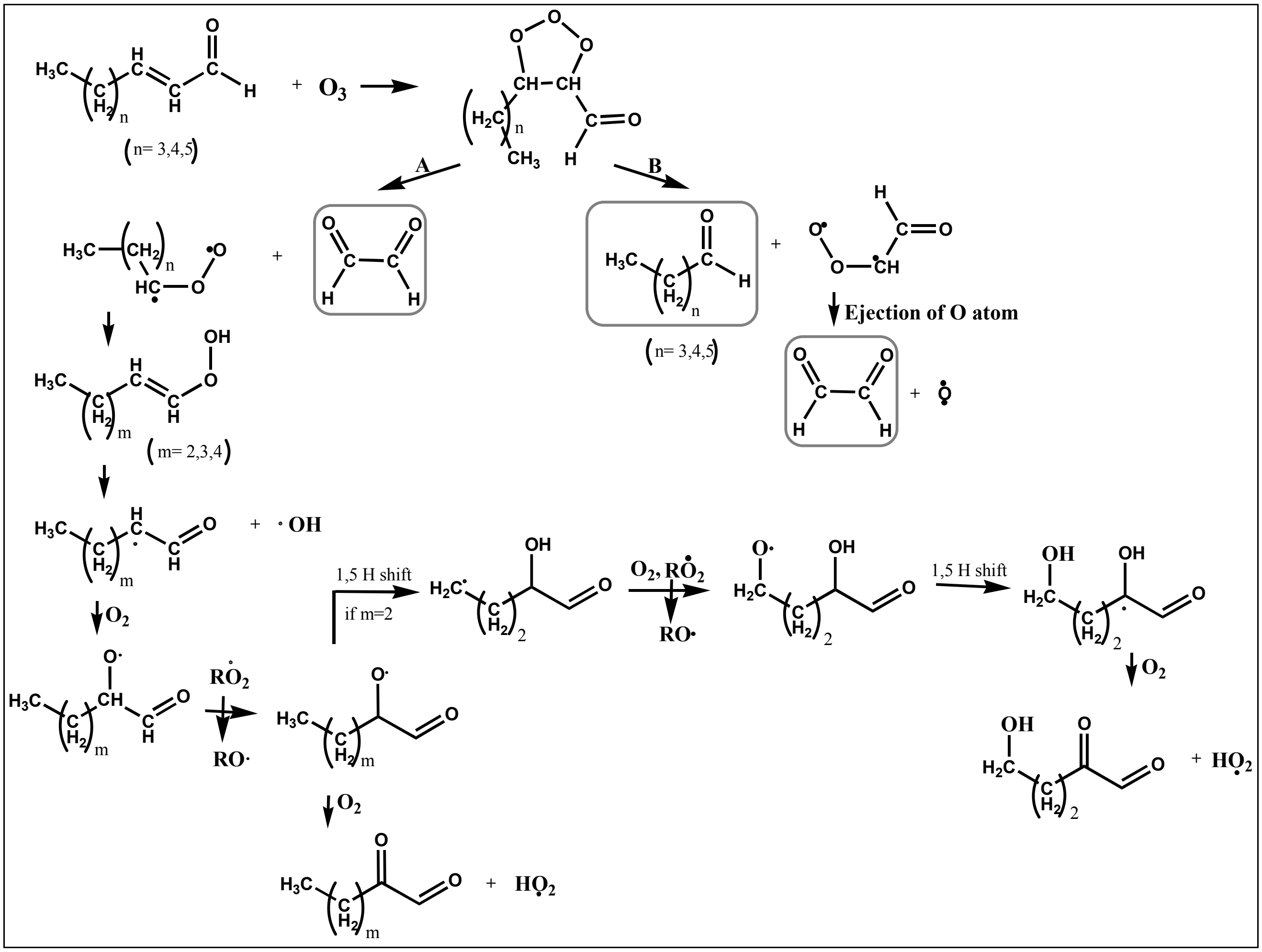

Figure 4: Simplified mechanism for the reaction of O_3 with *(E)*-2-heptenal, *(E)*-2-octenal and *(E)*-2-nonenal.

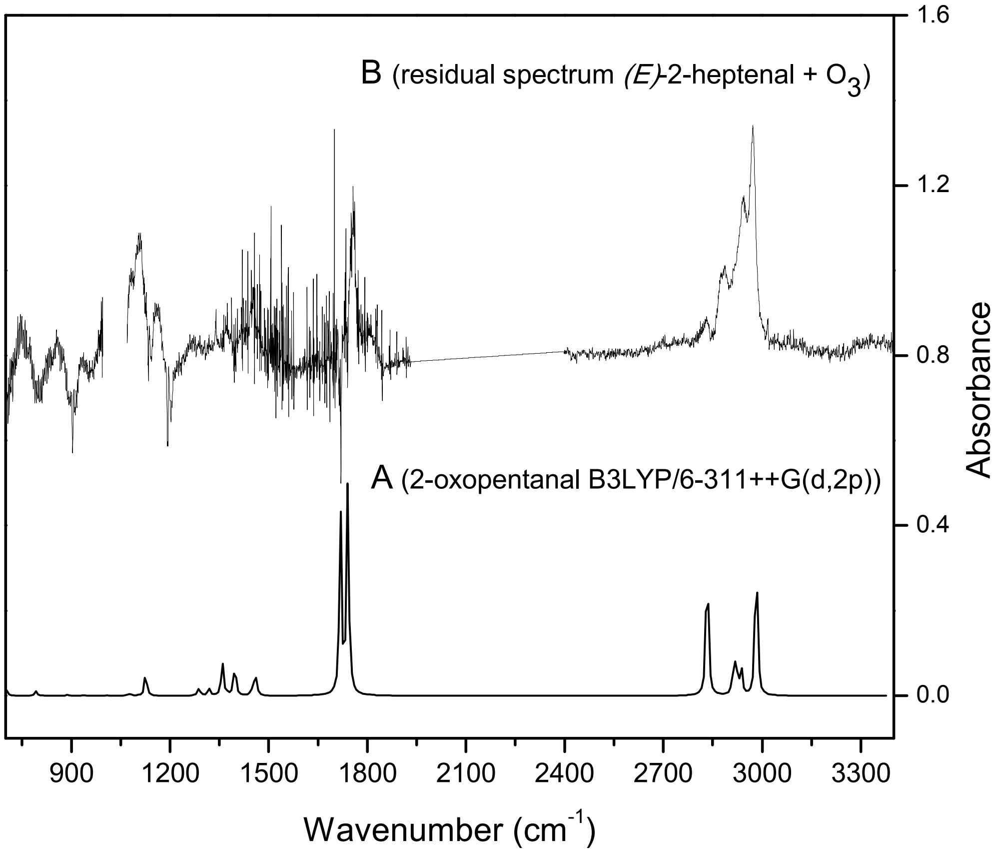

Figure 5: Comparison of a computed IR spectrum for the expected product 2-oxopentanal (A) with the residual product IR spectrum (B) obtained from an experiment with a *(E)*-2-heptenal/O_3/air mixture. (A straight line is presented between 1900-2400 cm^{-1} for the residual product spectrum avoiding the CO_2 and CO absorption)