

Gas-phase ozonolysis of β -ocimene: Temperature dependent rate coefficients and product distribution



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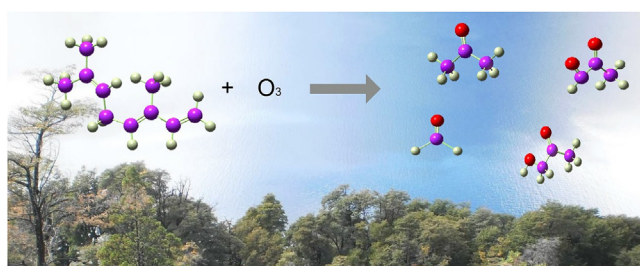
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HIGHLIGHTS

- First k temperature dependence below 298 K for the reaction of ozonolysis of β -ocimene.
- Rate coefficients increases with temperature with E_a/R 1181 K-1.
- Formation yields of hydroxyacetone and methylglyoxal reported for the first time.
- Direct formation of hydroxyacetone through isomerization/stabilization of biradical of Criegee.
- Ozonolysis of β -ocimene increases the atmospheric oxidative capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Rate coefficients for the reaction of β -ocimene with O₃ molecules have been determined over the temperature range 288–311 K at 750 Torr total pressure of nitrogen using the relative rate technique. The investigations were performed in a large volume reaction vessel using long-path in-situ Fourier transformed infrared (FTIR) spectroscopy to monitor the reactants and products. A value of $k(\beta\text{-ocimene} + \text{O}_3) = (3.74 \pm 0.92) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been obtained for the reaction at 298 K. The temperature dependence of the reaction is best described by the Arrhenius expression $k = (1.94 \pm 0.02) \times 10^{-14} \exp [(-1181 \pm 51)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In addition, a product study has been carried out at 298 K in 750 Torr of synthetic air and the following products with yields in molar % were observed: formaldehyde (36 ± 2), acetone (15 ± 1), methylglyoxal (9.5 ± 0.4) and hydroxyacetone (19 ± 1). The formation of formaldehyde can be explained by the addition of O₃ to the C₁–C₂ double bond of the β -ocimene. Addition of O₃ to the C₆–C₇ double bond leads to the formation of acetone and the CH₃C:(OO·)CH₃ biradical, which can through isomerization/stabilization form methylglyoxal (hydroperoxide channel) and hydroxyacetone. The formed products will contribute to the formation of PAN and derivatives in polluted environments and also the oxidation capacity of the atmosphere.

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1. Introduction

β -Ocimene is a monoterpene emitted into the atmosphere from biogenic sources (Guenther et al., 1994; Kesselmeier et al., 2000;

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Ortega et al., 2008; Song et al., 2014) the emission of which depends on several factors such as leaf temperature, light and even the chemical composition of the atmosphere (Kesselmeier and Staudt, 1999). Deciduous and mixed woodlands (Guenther et al., 1994) as well as tropical rainforests (Kesselmeier et al., 2000) are estimated to rank among the highest emitters of monoterpenes. In the troposphere, monoterpenes will react rapidly with OH radicals, NO₃ radicals and O₃ molecules because of the double bonds in their structure. Generally reaction with OH is the most important degradation pathway during the daytime and reaction with NO₃ during night, while the reaction O₃ can be an important degradation process during both daytime and nighttime depending on the prevailing O₃ levels. The products of these reactions are mainly multifunctional oxygenated compounds and many of the low volatility products can contribute to aerosol formation (Atkinson and Carter, 1984; Griffin et al., 1999; Finlayson-Pitts and Pitts, 2000; Russell et al., 2011).

There have been three previous studies on the kinetics of the reaction of O₃ with β-ocimene and isomers. Atkinson et al. (1990) have studied the reaction in a Teflon chamber at 296 K and 740 Torr total pressure of air using Gas Chromatography with a Flame Ionization Detector (GC/FID) for the analysis. Using a relative kinetic technique they obtained a value of $(5.56 \pm 0.85) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction. Also using a relative rate technique Witter et al. (2002) have determined the rate coefficient for the reaction at 295 K and 100 mbar total pressure in a quartz flow-tube using GC/FID for the analysis. They reported a value of $(5.5 \pm 0.8) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ that agrees very well with that of Atkinson et al. (1990). Kim et al. (2011) have studied the temperature dependence of the reaction of O₃ with β-ocimene over the range 298–318 K. They also used a relative kinetic technique and performed the investigations in a quartz reaction chamber using a quadrupole mass spectrometer (MS) operated in the electron impact (EI) mode to monitor the reactants. They report an Arrhenius expression for the reaction of $k = (3.15 + 1.36/-0.95) \times 10^{-15} \exp[-(626 \pm 110)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a value of $(3.85 + 0.30/-0.28) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction rate coefficient at 298 K. Sun et al. (2011) have performed a theoretical study using molecular orbital theory for the kinetics and the chemical mechanism in the presence of H₂O or NO on the ocimene ozonolysis reaction. The authors have presented the rate coefficients for elementary reactions over the temperature range 200–800 K.

There have been some previous product studies on the reaction of O₃ with β-ocimene and also on the reaction of O₃ with the structurally-related compound myrcene. The formation yield of acetone in the ozonolysis of β-ocimene at 298 K and atmospheric pressure of air has been reported by Reissell et al. (1999) who studied the reaction in a Teflon chamber using GC/FID and GC/MS for the analysis. Acetone is one of the carbonyl compounds expected to be formed from addition of O₃ to the $-\text{CH}=\text{C}(\text{CH}_3)_2$ moiety in β-ocimene. In a follow-up study using similar techniques Reissell et al. (2002) not only confirmed the previous acetone yield but also detected and quantified the formation of 4-methyl-3,5-hexadienal the other expected carbonyl compound from the addition of O₃ to the $-\text{CH}=\text{C}(\text{CH}_3)_2$ moiety in β-ocimene.

For the reaction of O₃ with the structurally-related compound myrcene, Ruppert et al. (1999) have reported the formation of hydroxyacetone, formaldehyde and acetone as products with molar yields of 19, 26 and 29%, respectively. The experiments were performed in a large volume quartz reactor using *in-situ* long-path FTIR to monitor reactants and products. More recently, Böge et al. (2013) have investigated the reaction of O₃ with myrcene in an aerosol chamber between 292 and 295 K using proton transfer reaction mass spectrometry (PTR-MS) for the analysis. They

observed a high yield of 4-vinyl-4-pentenal (55.3%) and the formation of two different organic dicarbonyls whose yields varied in the presence and absence of an OH radical scavenger. They also observed the direct formation of hydroxyacetone with a yield of 17.6% in good agreement with the study of Ruppert et al. (1999).

In this work, we present rate coefficients for the reaction of β-ocimene with O₃ molecules measured at 750 Torr total pressure of nitrogen over the temperature range 288–311 K. The investigations extend the previous temperature dependence of the reaction by Kim et al. (2011) to temperatures below 298 K and serve as a validation of their results. Additionally, the products of the ozonolysis of β-ocimene have been investigated at 298 K and 750 Torr total pressure of synthetic air using *in-situ* long path FTIR for the analysis. From this work we report for the first time the formation yields of methylglyoxal and the direct formation of hydroxyacetone from the β-ocimene ozonolysis reaction. This contribution will help to understand the atmospheric chemical mechanisms of monoterpenes and the influence they have on the oxidative capacity of the troposphere.

2. Experimental section

The experiments were performed in a 1080 L reactor. The reactor consists of two cylindrical quartz glass vessels, each 3 m in length and 45 cm inner diameter, joined in the middle with both opened ends closed by aluminium flanges. The metal flanges contain ports for the introduction of bath gases and reactants into the chamber. To ensure homogeneous mixing of the reactants three fans with Teflon blades are mounted inside the reactor. The reactor can be evacuated by a pumping system, consisting of a turbomolecular pump backed by a double stage rotary fore pump, to 10⁻³ Torr. A White-type mirror system is disposed internally in the chamber and coupled to a FTIR spectrometer (Thermo Nicolet Nexus). The spectrometer is equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector, which enables "*in situ*" monitoring of the reactants in the infrared range 4000–700 cm⁻¹. The "White" mirror system in the reactor was operated with the total optical absorption path length set to 484.7 m. The reactor is equipped with a system for temperature regulation over the range 284–313 K with a precision of ±1 K. The reactor is described in greater detail in Barnes et al. (1993, 1994).

For the kinetic experiments ozone, produced by flowing O₂ through an electrical discharge, was added stepwise to ppm mixtures of β-ocimene and the reference compound in 750 Torr of nitrogen. Typically, 30 interferograms were co-added per spectrum and 15 such spectra were recorded during the course of the experiment. The kinetic experiments were performed over the temperature range 288–311 K.

The products formed in the reaction of O₃ molecules with β-ocimene were investigated by adding ozone continuously to β-ocimene in synthetic air while simultaneously recording infrared spectra with the FTIR spectrometer. Typically 30 interferograms were co-added per spectrum and 20 such spectra collected. All the infrared spectra were recorded with a spectral resolution of 1 cm⁻¹. Both the kinetic and product experiments were performed in the absence of an OH radical scavenger the consequences of which are discussed later.

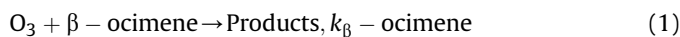
Reactants and products were quantified by comparison with calibrated reference spectra contained in the IR spectral databases of the laboratories in Wuppertal and The Centro de Estudios Ambientales del Mediterráneo (CEAM) Foundation in Valencia, Spain. The reactants were monitored at the following infrared absorption frequencies (in cm⁻¹): β-ocimene 2700–3150; *t*-2-butene 963; α-pinene 2826–3052. Identified reaction products were monitored at the following infrared absorption frequencies (in

cm^{-1}): acetone 1217; formaldehyde 2766; methylglyoxal 2835; hydroxyacetone 1107.

The initial concentrations of the organic compounds in ppmV (1 ppm V = 2.46×10^{13} molecule cm^{-3} at 298 K) were approximately: β -ocimene 2.7–3; *t*-2-butene 2.3–2.5; α -pinene 1.9–2.2. The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: nitrogen (Air Liquide, 99.999%), synthetic air (Air Liquide, 99.999%), β -ocimene mixture of isomers (Aldrich, $\geq 90\%$), (*E*)-2-butene (Messer Griesheim, 99%) and α -pinene (Aldrich 98%).

3. Results and discussion

The relative rate technique has been used to determinate the rate coefficients for the reaction of O_3 molecules with β -ocimene as a function of temperature. In this method the rate of decay of β -ocimene is compared with the corresponding decay of a reference compound with a well-established ozonolysis rate coefficient:



Assuming that β -ocimene and the reference compound are lost only by reactions (1) and (2) then it can be shown that:

$$\ln \left\{ \frac{[\beta\text{-ocimene}]_0}{[\beta\text{-ocimene}]_t} \right\} = \frac{k_{\beta\text{-ocimene}}}{k_{\text{reference}}} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (1)$$

where $[\beta\text{-ocimene}]_0$, $[\text{reference}]_0$, $[\beta\text{-ocimene}]_t$ and $[\text{reference}]_t$ are the concentrations of the studied and reference compounds at times $t = 0$ and t , respectively, and $k_{\beta\text{-ocimene}}$ and $k_{\text{reference}}$ the rate coefficients of reactions (1) and (2), respectively.

The relative rate technique is based on the assumption that β -ocimene and the reference compound are removed solely by reaction with the O_3 molecules. No significant loss of β -ocimene and the reference compounds was observed on leaving mixtures of the compounds in the bath gas to stand over 30 min showing that loss through deposition on the reactor surface was negligible for all the substances. However, the ozonolysis of β -ocimene and the reference compounds is known to produce OH radicals which could influence the kinetic measurements. This point is discussed in detail below.

(*E*)-2-Butene was employed as the reference compound for the study of the temperature dependence of the reaction over the range 288–311 K. The following Arrhenius expression $k_{\text{O}_3} = 6.64 \times 10^{-15} \exp(-1059/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997; Atkinson and Arey, 2003) was used to calculate the rate coefficients for the reaction of O_3 with (*E*)-2-butene at the appropriate experimental temperatures. As a check on the results using (*E*)-2-butene as the reference compound and also to highlight possible artefacts in the measurements, α -pinene, with a rate coefficient of $k_{\text{O}_3} = (8.4 \pm 1.9) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Carter, 1984), was used as a reference compound to determine the rate coefficient for the reaction of O_3 with β -ocimene at 298 K.

Fig. 1 shows the kinetic data, plotted according to eq. (1), obtained from experiments on the reactions of β -ocimene with O_3 molecules at 298 K measured relative to the reference compounds α -pinene and (*E*)-2-butene. Each plot represents three experiments for each reference compound. As seen from Fig. 1 linear relationships were obtained in all experiments. The rate coefficient ratios $k_{\beta\text{-ocimene}}/k_{\text{reference}}$ obtained from the individual plots from each experiment are listed in Table 1 together with the absolute values of the rate coefficients for the reactions of β -ocimene with O_3 molecules at 298 K calculated using the appropriate temperature rate

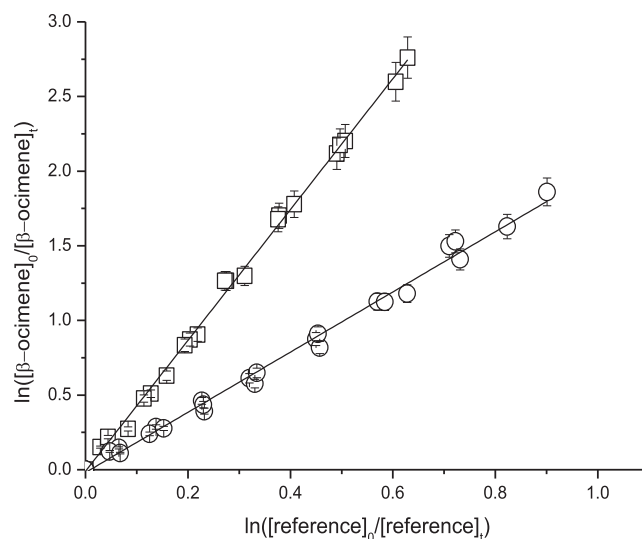


Fig. 1. Plot of the kinetic data for the reaction of O_3 molecules with β -ocimene measured relative. To (*E*)-2-butene (\circ) and α -pinene (\square) at 298 ± 2 K and 750 ± 10 Torr.

coefficient values for the reference reactions. Since the values of the rate coefficients obtained in the individual measurements with each reference compound, and also the values obtained with both reference compounds, are in such good agreement we prefer to quote a final rate coefficient for the reaction of O_3 with β -ocimene at 298 K which is the average of all the determinations:

$$k_{(\beta\text{-ocimene} + \text{O}_3)} = (3.74 \pm 0.92) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines plus a contribution of the uncertainties in the reference rate coefficients.

As stated in the Experimental section, the experiments were performed in absence of an OH radical scavenger although it is known that the ozonolysis of unsaturated compounds produces OH radicals, which can interfere with the type of relative kinetic and product studies presented here. The rate coefficient for the reaction of OH with β -ocimene is near the gas kinetic limit (Atkinson and Arey, 2003), thus enormously high concentrations of a scavenger would be necessary to effectively scavenge any OH radicals produced in the reaction system. Such high concentrations of an OH-radical scavenger in our reaction system, such as CO, would render monitoring of the reactants in the infrared very difficult quite aside from the safety issues with such large quantities of CO in our voluminous reaction chamber.

In an attempt to lessen the potential extent of the impact of OH radicals on the kinetic measurements, the experiments have been performed in nitrogen. Apart from this measure we argue below, based on the results, that the extent of OH radical interference on the present kinetic results is not significant.

The rate coefficients obtained at 298 K for the reaction of O_3 with the β -ocimene using two reference compounds, (*E*)-2-butene and α -pinene, are in excellent agreement with one another. The rate coefficients for the reaction of O_3 with (*E*)-2-butene and α -pinene differ by a factor of just over 2, therefore, any significant influence of OH radical chemistry on the results should have led to a pronounced discrepancy in the results for the two reference compounds. The rate coefficient for the reaction of OH radicals with β -ocimene is approximately factors of 4 and 5 higher those of the corresponding reactions with (*E*)-2-butene and α -pinene, respectively. Therefore, any OH produced in the reaction system will

Table 1

Rate coefficient ratios $k_{\text{ocimene}}/k_{\text{reference}}$ and absolute rate coefficients obtained for the reaction of O_3 molecules with β -ocimene from experiments performed at 298 K in 750 ± 10 Torr of nitrogen.

Reference	$k_{\text{ocimene}}/k_{\text{reference}}$	$k_{\text{ocimene}} \times 10^{16}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
(<i>E</i>)-2-butene	2.037 ± 0.036	3.87 ± 0.84
(<i>E</i>)-2-butene	1.896 ± 0.054	3.60 ± 0.82
(<i>E</i>)-2-butene	2.052 ± 0.069	3.90 ± 0.91
α -pinene	4.391 ± 0.076	3.69 ± 0.89
α -pinene	4.406 ± 0.105	3.70 ± 0.92
α -pinene	4.393 ± 0.055	3.69 ± 0.88
Average:		3.74 ± 0.92

primarily affect the decay of β -ocimene and potentially lead to too high values of the rate coefficient compared to other literature studies were the measurements were performed in the presence of an OH-radical scavenger (Atkinson et al., 1990; Kim et al., 2011; Witter et al., 2002). The rate coefficient obtained in this study at 298 K for the reaction of β -ocimene with O_3 molecules of $(3.74 \pm 0.92) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in excellent agreement with the value of $(3.85^{+0.30}_{-0.28}) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Kim et al. (2011) for 296 K. On the other hand, the rate coefficient at 298 K measured in this work is $\sim 33\%$ lower than the room temperature values of $(5.56 \pm 0.85) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(5.5 \pm 0.8) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Atkinson et al. (1990) and Witter et al. (2002), respectively. However, considering the experimental difficulties and errors in measuring slow ozonolysis rate coefficients this agreement can still be viewed as satisfactory.

The temperature dependence of the reaction of O_3 molecules with β -ocimene was studied over the temperature range 288–311 K using (*E*)-2-butene as reference compound. Rate coefficients for the reaction of β -ocimene with O_3 molecules as a function of temperature have been derived from linear least-squares analysis of plots of the kinetic data according to eq (I) for 288, 293, 298, 303 and 311 K (Figures are shown in supplementary information) and the average values are listed in Table 2 and depicted in Arrhenius form in Fig. 2.

The following Arrhenius expression was obtained from a linear regression analysis of the Arrhenius plot in Fig. 2:

$$k_{(\text{O}_3+\beta\text{-ocimene})}(T) = (1.94 \pm 0.17) \times 10^{-14} \exp[(1181 \pm 51)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation from a least-squares fit to the data points plus an additional 20% to account for the uncertainty in the temperature dependence of the rate coefficient for (*E*)-2butene.

The reaction exhibits a slightly positive Arrhenius behavior, i.e. the rate coefficients increase with increasing temperature over the range 288–311 K. Kim et al. (2011) have also measured the temperature dependence of the reaction over the temperature range 298–318 K. Points calculated using the Arrhenius expression reported by Kim et al. (2011) are plotted in Fig. 2. As can be seen in

Table 2

Rate coefficients and Arrhenius parameters for the reactions of O_3 molecules with β -ocimene over the temperature range 288–311 K measured in 750 ± 10 Torr of nitrogen.

Temperature	$k_{\text{ocimene}} \times 10^{16}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$-E_a/R$ (K)	$A \times 10^{14}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
288 K	3.20 ± 0.70	-1181 ± 51	1.94 ± 0.17
293 K	3.42 ± 0.72		
298 K	3.74 ± 0.92		
303 K	3.92 ± 0.84		
311 K	4.33 ± 1.00		

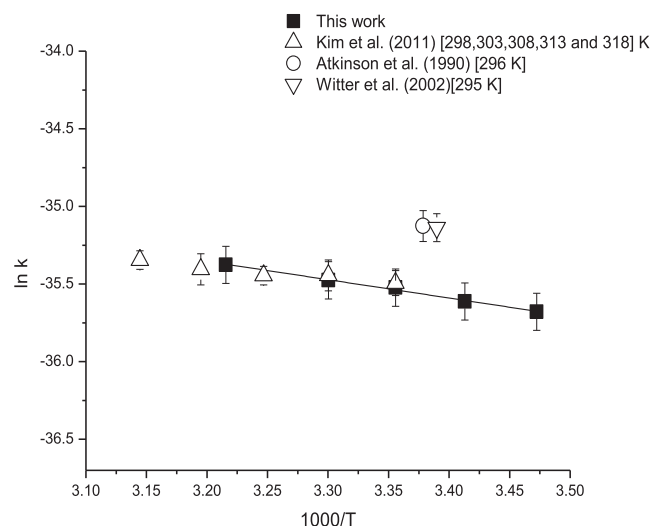


Fig. 2. Arrhenius plot of the kinetic data for the reaction of O_3 molecule with β -ocimene over the temperature range 288–311 K from this work and a comparison with values of the rate coefficient available in the literature.

Fig. 2 the Arrhenius behavior determined by Kim et al. (2011) agrees well with that determined in this study. This study, however, seems to indicate a somewhat stronger temperature dependence than that measured by Kim et al. (2011). The somewhat higher room temperature values of the rate coefficient determined by Atkinson et al. (1990) and Witter et al. (2002) are also shown in Fig. 2 for comparison.

Our value of E_a/R for the ozonolysis of β -ocimene is approximately double that reported by Kim et al., 2011 but it is approximately the same as the value they measure for the ozonolysis of the structurally similar compound myrcene. The values of E_a/R reported in the literature data for the reactions of O_3 molecules with alkenes containing conjugated double bonds generally fall in the approximate range 1000–2700 K. Values of 2283, 1913, 1668 and 1158 K have been reported for the reactions of O_3 molecules with 1,3-butadiene; 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene (Atkinson, 1997; Atkinson and Arey, 2003), respectively. The E_a/R value of 1181 K reported in this work for the reaction of β -ocimene with O_3 is therefore consistent with the available literature data.

3.1. Product studies

The ozonolysis of alkenes proceeds via a complex series of reactions and intermediates. The reaction is initiated by addition of O_3 molecules to the double bond(s) of the unsaturated compound to form a five-membered ring intermediate species known as a primary ozonide. The ozonide formation process is highly exothermic and this excess of energy leads to decomposition of the primary ozonide. The decomposition leads to formation of an aldehyde/ketone and a chemically activated carbonyl oxide, known

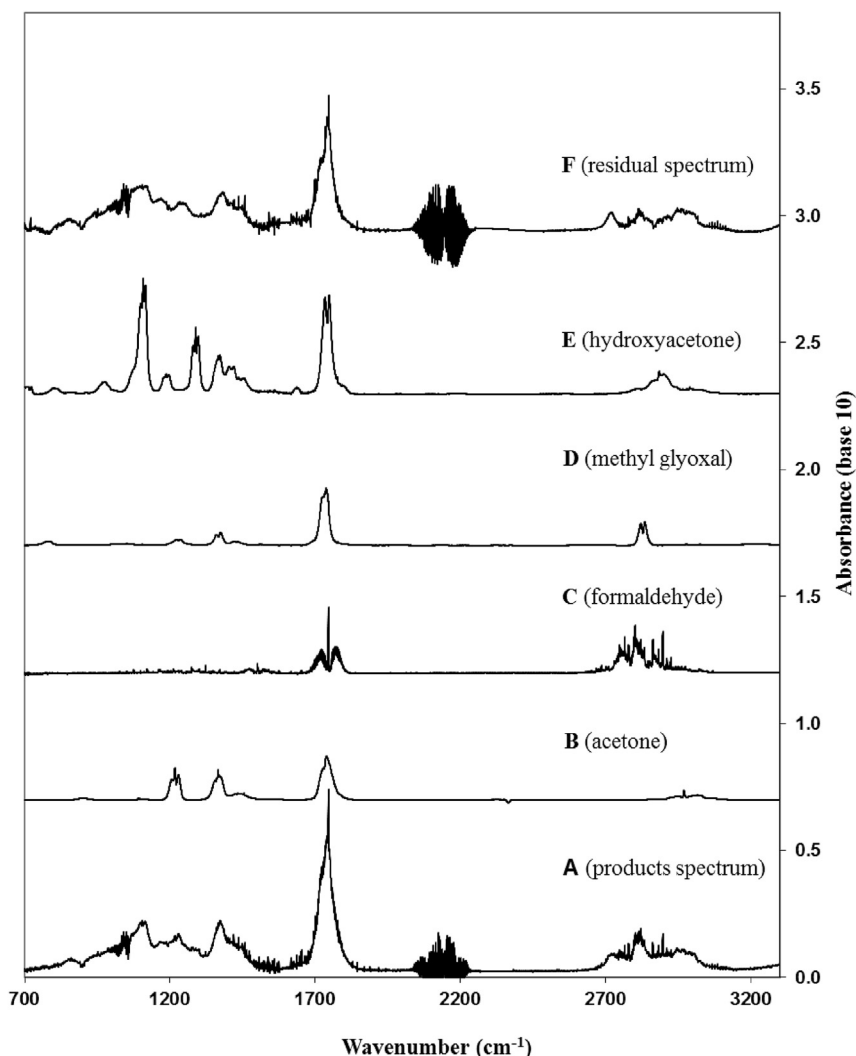


Fig. 3. Panel A shows the infrared product spectrum obtained from a β -ocimene/ O_3 /air reaction mixture. Panels B, C and D show reference spectra of acetone, formaldehyde and methylglyoxal, respectively. Panel E shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A.

as a Criegee intermediate (CI), which can undergo unimolecular decomposition, isomerization or can be stabilized by collision with the bath molecules. (Horie and Moortgat, 1998). It is now well established that ozonolysis reactions form OH radicals, through the isomerization of the Criegee biradical via the so called hydroperoxide channel (Atkinson, 1997; Calvert et al., 2000, 2015).

Fig. 3, panel A, shows the infrared product spectrum obtained from a β -ocimene/ O_3 /air reaction mixture after subtraction of residual β -ocimene. Panels B, C, D and E show reference spectra of acetone ((CH_3) $_2$ C=O), formaldehyde (HCHO), methylglyoxal ($CH_3C(O)CHO$) and hydroxyacetone (CH_3COCH_2OH). Panel F shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A. Formation of acetone, formaldehyde, methylglyoxal and hydroxyacetone was positively identified. Concentration-time profiles of β -ocimene and the identified products are presented in Fig. 4 and the shape of the curves supports that the products acetone, formaldehyde, methylglyoxal and hydroxyacetone are all either totally or mainly primary in origin. Plots of the concentrations of acetone, formaldehyde, methylglyoxal and hydroxyacetone as a function of consumed β -ocimene are shown in Fig. 5 and all show reasonable linearity. The average product yields that have obtained from two

experiments are shown in Table 3. (The product yields of each experiment are shown in supplementary information).

Structure-activity relationships for predicting rate coefficients for the reaction of O_3 with monalkenes and dienes (King et al., 1999; McGillen et al., 2008) predict that $\sim 58\%$ of the O_3 will add at the $>C=C<$ entity in β -ocimene and $\sim 42\%$ at the conjugated diene entity.

Figs. 6 and 7 show simplified mechanisms of for the addition of O_3 to the $C_1=C_2$ and $C_6=C_7$ double bond entities in β -ocimene. Addition at the $C_1=C_2$ double bond generates an ozonide, which can decompose through two channels, A and B (Fig. 6). Decomposition of the ozonide through channel A forms formaldehyde and the Criegee biradical $CH_3C(CH_3)=CHCH_2CH=C(CH_3)C\cdot H(OO\cdot)$ while decomposition through channel B can form the aldehyde $CH_3C(CH_3)=CHCH_2CH=C(CH_3)C(O)H$ and the corresponding Criegee biradical $\cdot CH_2OO\cdot$. A yield of $(36 \pm 2)\%$ has been obtained for formaldehyde, the other aldehyde could not be identified due to lack of an authentic sample of the compound. To the best of our knowledge, the yield of formaldehyde for the reaction of β -ocimene with O_3 reaction has not been previously reported. However, Ruppert et al. (1999) have reported a yield of 26% for formaldehyde formation in the ozonolysis of the structurally similar compound

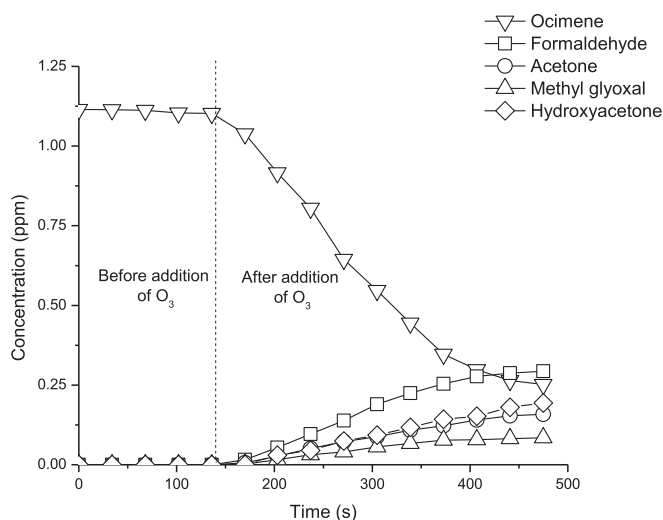


Fig. 4. Concentration-time profiles of β -ocimene and the reaction products formaldehyde, acetone, methylglyoxal and hydroxyacetone obtained from a β -ocimene/ O_3 /air reaction mixture.

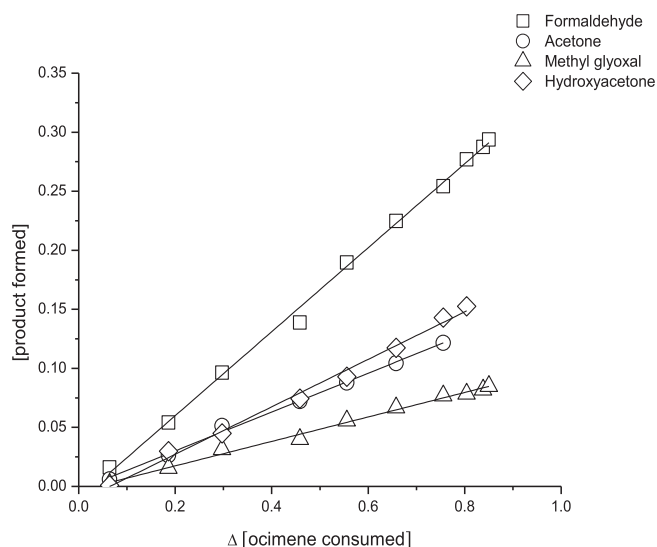


Fig. 5. Plots of the concentrations of the reaction products formaldehyde, acetone, methylglyoxal and hydroxyacetone as a function of reacted β -ocimene obtained from experiments performed on β -ocimene/ O_3 /air reaction mixtures.

Table 3

Formation yields of the oxidation products identified in the ozonolysis of β -ocimene at 298 K in 750 ± 10 Torr of air without an OH radical scavenger.

Product	Yield (%)
HC(O)H Formaldehyde	36 ± 2
CH ₃ C(O)CH ₃ Acetone	15 ± 1
CH ₃ C(O)C(O)H Methylglyoxal	9.5 ± 0.4
HOCH ₂ C(O)CH ₃ Hydroxyacetone	19 ± 1

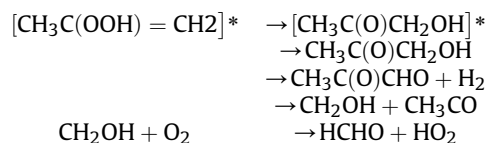
myrcene. Addition of O_3 to the $C_1=C_2$ double bond in β -ocimene is not the only possible source of formaldehyde, as is discussed below, reaction pathways after addition at the $C_6=C_7$ position can also lead to formaldehyde formation.

Addition of O_3 at the $C_6=C_7$ double bond in β -ocimene again forms an ozonide, which can decompose via two channels A and B

(Fig. 7). Decomposition of the ozonide through channel A can form acetone and the $CH_2=CHC(CH_3)=CHCH_2C\cdot H(OO\cdot)$ biradical. Acetone formation has been observed in our experiments with a yield of (15 ± 1) %. Reissell et al. (1999, 2002) have reported an acetone yields of (21 ± 4) % and (24 ± 4) % for the ozonolysis of β -ocimene at room temperature and a total pressure of 740 Torr, respectively. Considering the difficulties involved in ozonolysis product experiments the agreement in acetone yields between the studies can be considered reasonable.

Decomposition of the ozonide through channel B can form the aldehyde $CH_2=CHC(CH_3)=CHCH_2C(O)H$ and the chemically activated Criegee biradical $[(CH_3)_2C\cdot(OO\cdot)]^*$. The fragmentation pattern of the excited $[(CH_3)_2C\cdot(OO\cdot)]^*$ biradical has been studied using different alkene- O_3 reactions to produce the biradical and are summarized in Calvert et al. (2000, 2015). Major products observed in the studies included CO, CO₂, HCHO, acetone $(CH_3)_2C=O$, $CH_3C(O)CHO$ and $CH_3C(O)CH_2OH$ (Niki et al., 1987; Martinez and Herron, 1987; Calvert et al., 2000). Niki et al. (1987) showed that a major fate of the excited $[(CH_3)_2C\cdot(OO\cdot)]^*$ biradical is isomerization to form the excited hydroperoxide $[CH_3C(OOH)=CH_2]^*$ intermediate. Dissociation of the hydroperoxide can form OH and $CH_3C(O)CH_2\cdot$ radicals. If formed the $CH_3C(O)CH_2\cdot$ radicals will add O_2 to form a peroxy radicals the further peroxy-peroxy reactions of which can lead to formation of hydroxyacetone, methylglyoxal and HCHO.

However, various other channels for the decomposition of $[CH_3C(OOH)=CH_2]^*$ have been proposed (Calvert et al., 2000, 2015) which could lead to formation of hydroxyacetone, methylglyoxal and HCHO:



The isomerization of the excited $[(CH_3)_2C\cdot(OO\cdot)]^*$ biradical to form the excited hydroperoxide is shown pictorially in Fig. 7, channel B1, along with its further reactions to form methylglyoxal and hydroxyacetone through channels B₁₁ and B₁₂, respectively.

The yield of hydroxyacetone obtained in this work is (19 ± 1) % and that of methylglyoxal is (9.5 ± 0.4) %. To the best of our knowledge, the formation yields of hydroxyacetone and methylglyoxal for the ozonolysis of β -ocimene have not been previously reported. However, yields of 19% and 17.6% have been reported for hydroxyacetone formation by Ruppert et al. (1999) and Böge et al. (2013), respectively for their product studies on the ozonolysis of myrcene. Taking into account the similarity in structure between β -ocimene and myrcene, the yield of hydroxyacetone obtained in this work seems to be of the size that one would expect for an acyclic monoterpene with a conjugated double bond system.

In product studies in this laboratory on the reaction of OH radicals with β -ocimene we have not observed hydroxyacetone as a reaction product. This observation infers that hydroxyacetone is a direct reaction product in the ozonolysis of β -ocimene and is not formed via secondary reactions with OH radicals. Further support for this thesis comes from the work of Böge et al. (2013, 2014) who concluded from their ozonolysis studies on myrcene, ocimene and terpinolene performed in the presence of an OH radical scavenger that the hydroxyacetone formation they observed in these reactions was the result of a direct formation process and not through reaction of the compounds with OH.

Working on the premise that the sum of the yields of the carbonyls formed from the two possible splitting routes of a primary ozonide formed from the reaction of O_3 with an alkene is unity the

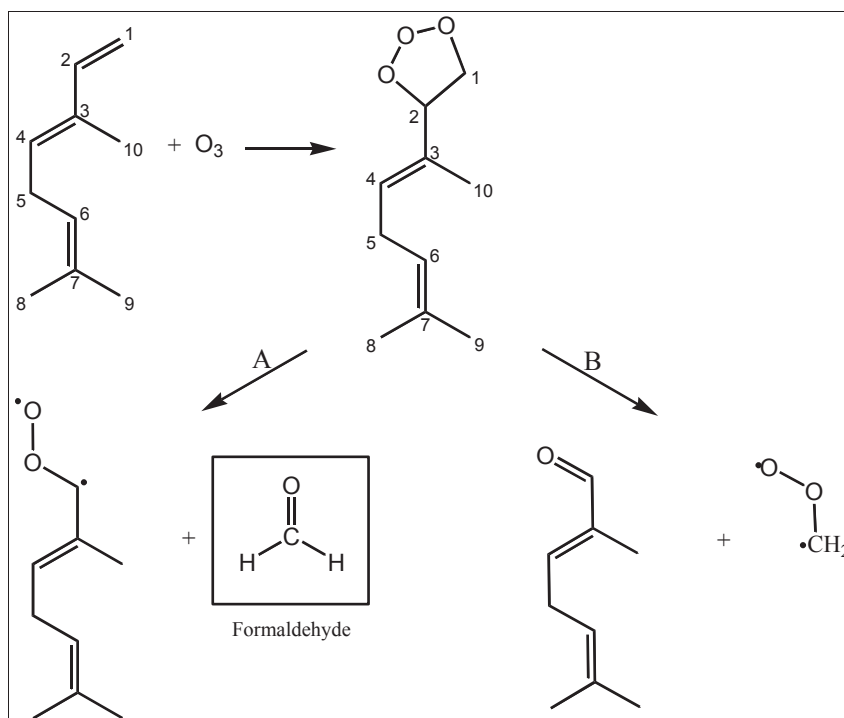


Fig. 6. Simplified mechanism for the reaction of β -ocimene with O_3 molecules via addition of O_3 to the double bond binding C_1 and C_2 .

following observations can be made. The SAR of King et al. (1999) predicts that approximately 58% of the reaction proceeds by O_3 addition at the $(CH_3)_2C=CH-$ entity in β -ocimene which based on the premise translates to a total aldehyde/ketone yield of ~58% for O_3 addition at the double bond. The sum of the yields of acetone, hydroxyacetone and methylglyoxal which are formed through addition of O_3 to the $(CH_3)_2C=CH-$ entity is ~44%. This is ~14% short of the yield sum required to match the SAR prediction of 58%, however, as discussed above formation of HCHO via addition of O_3 at the $C_6=C_7$ double bond can also occur. Unfortunately, it is impossible to say how much of the total HCHO yield of 36% is attributable to O_3 addition at the $C_1=C_2$ double bond and how much at the $C_6=C_7$. The $C_1=C_2$ double bond in β -ocimene can be viewed as a mono-substituted alkene where it is known that the formation ratio of the two possible Criegee biradicals is approximately 50:50 (Calvert et al., 2000). Since quite a large proportion of the O_3 attack at the conjugated double bond system in β -ocimene will be at the $C_3=C_4$ double bond it is quite probable that the percentage of the total HCHO yield originating from O_3 reaction at the $C_1=C_2$ double bond is a good deal less than 100%.

The $(CH_3)_2C=CH-$ entity in β -ocimene can be classified as a trisubstituted alkene. For this type of alkene it is known that the primary ozonide decomposes preferentially to form the disubstituted biradical, i.e. in the case of $R_1R_2C=CH_2$ this would be $[R_1R_2C\cdot(OO\cdot)]^*$ + HCHO (Calvert et al., 2000). The results obtained here for the ozonolysis of β -ocimene also show this trend. The combined yields of methylglyoxal and hydroxyacetone of 28.5% is nearly twice the yield acetone showing that reaction of O_3 at the $C_6=C_7$ double bond in β -ocimene results preferentially in the formation of the disubstituted activated biradical $[(CH_3)_2C\cdot(OO\cdot)]^*$.

Although, addition of O_3 to the $C_3=C_4$ double bond in β -ocimene is also possible we were unable to identify any products that could be forming through this addition pathway. Decomposition of the ozonide after addition at $C_3=C_4$ could form methyl vinyl ketone and 4-methyl-3-pentenal and the corresponding Criegee biradicals.

3.2. Atmospheric implications

The kinetic data obtained in this work at 298 K has been used to determine the lifetime of β -ocimene due to reaction with O_3 molecules. This lifetime is compared with the lifetimes due to the reaction of the compound with the other atmospheric oxidants OH and NO_3 radicals using the available literature rate coefficients for their reactions with β -ocimene. The calculated lifetimes are given in Table 4. The lifetimes have been calculated using the expression $\tau_x = 1/k_x [X]$ with $X = OH, O_3$ or NO_3 , k_x is the rate coefficient for the reaction of the oxidant X with β -ocimene and $[X]$ is the atmospheric concentration of the oxidant: $[OH] = 2 \times 10^6$ radical cm^3 (Hein et al., 1997), $[O_3] = 7 \times 10^{11}$ molecule cm^3 (Logan, 1985) and $[NO_3] = 5 \times 10^8$ radical cm^3 (Shu and Atkinson, 1995). Not unexpectedly, the lifetimes indicate that the residence time of β -ocimene in the troposphere due to reaction with the atmospheric oxidants is very short with reaction with OH dominating during the daytime and NO_3 during the night. However, in polluted areas with high O_3 levels the reaction of O_3 molecules with β -ocimene will also contribute significantly to its loss during the daytime. These very short atmospheric lifetimes of β -ocimene show that the degradation of β -ocimene occurs quite close to its emission sources.

The product study has shown that the ozonolysis of β -ocimene is a source of formaldehyde, acetone, methylglyoxal, hydroxyacetone and other unidentified unsaturated oxygenates all of which will be subject to further degradation with the main atmospheric oxidants. The photolysis of HCHO is a source of OH radicals and acetone is a very relevant atmospheric source of HO_x radicals and peroxyacetyl nitrate (PAN) (Müller and Brasseur, 1999; Fischer et al., 2014). The model simulations of Khan et al. (2015) suggest that the monoterpenes account for 64% (46.8 Tg/yr) of the global acetone sources. Spaulding et al., 2003 have determined the mixing ratios of methylglyoxal and hydroxyacetone over a ponderosa pine plantation. The authors found that the mixing ratio of methylglyoxal was lower than that of hydroxyacetone, which is expected due to the shorter lifetime of methylglyoxal which is degraded by

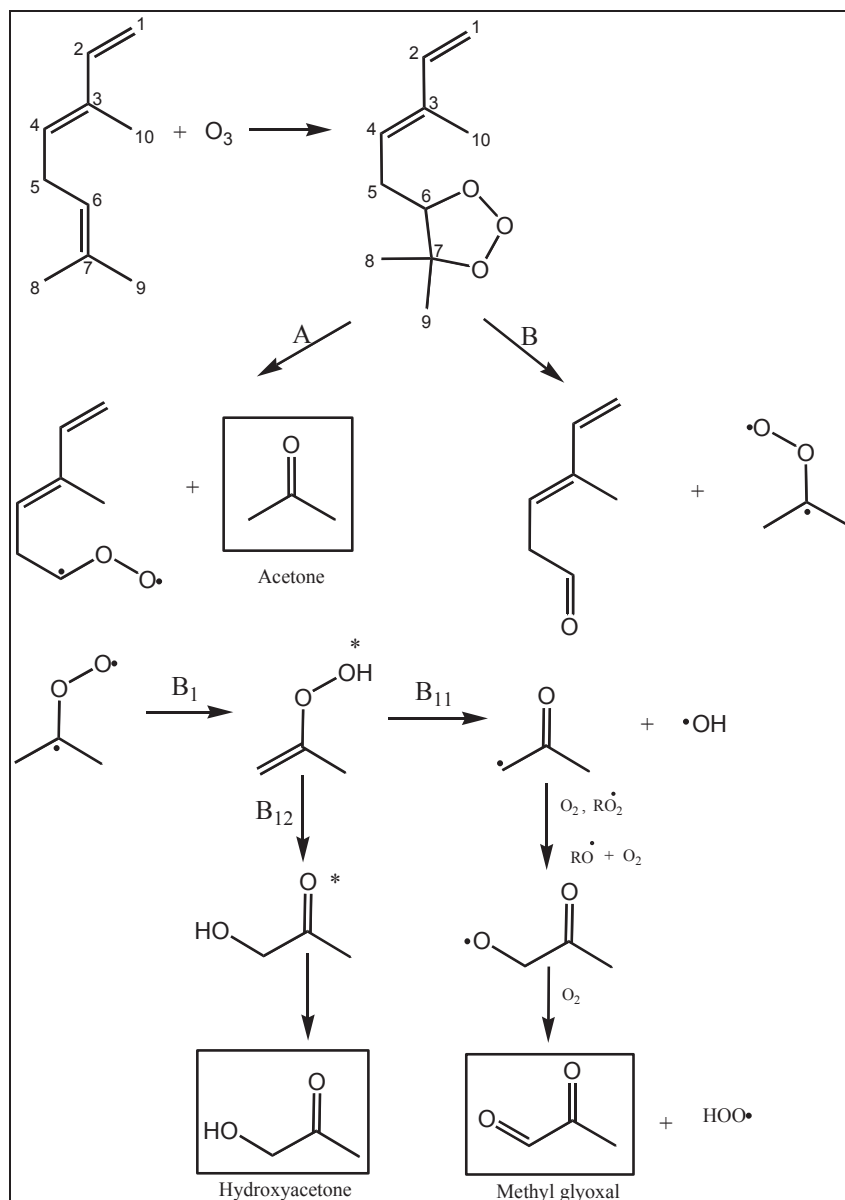


Fig. 7. Simplified mechanism for the reaction of β -ocimene with O_3 molecules via addition of O_3 to the double bond binding C_6 and C_7 .

Table 4

Atmospheric lifetimes of β -ocimene with respect to its reactions with O_3 , OH and NO_3 .

k_{OH} ($cm^3 \text{ molecule}^{-1} s^{-1}$)	τ_{OH} (min)	k_{O_3} ($cm^3 \text{ molecule}^{-1} s^{-1}$)	τ_{O_3} (min)	k_{NO_3} ($cm^3 \text{ molecule}^{-1} s^{-1}$)	τ_{NO_3} (min)
2.50×10^a	33	3.85×10^{-16b}	62	2.40×10^{-11e}	1
		5.56×10^{-16c}	43		
		3.74×10^{-16d}	64		

^a Atkinson et al. (1986).

^b Kim et al. (2011).

^c Atkinson et al. (1990).

^d This work.

^e Atkinson et al. (1985).

photolysis and reaction with OH. In contrast, the hydroxyacetone has longer lifetime hence, its atmospheric implications can be important on a regional scale.

4. Conclusions

An experimental investigation of the kinetics and products

formed in the gas-phase reaction of ozone with β -ocimene, a monoterpene that contains three double bonds, has been performed. The rate coefficient obtained at room temperature in this work for the reaction is in reasonable agreement with previous values reported in the literature even though the experiments were performed in the absence of an OH radical scavenger. Additionally, a temperature dependent study of the reaction has provided new

kinetic data below room temperature. The product study has shown that the ozonolysis of β -ocimene is an important source of formaldehyde, methylglyoxal and hydroxyacetone. The products yields are very similar to those reported in the literature for the structurally comparable compound myrcene.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.09.053>.

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