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Effect of NO_x on product yields and Arrhenius parameters of gas-phase oxidation of β-ocimene initiated by OH[•] radicals†

 Elizabeth Gaona-Colmán,^a María B. Blanco,^a Ian Barnes^b and Mariano A. Teruel^{*a}

Rate coefficients for the gas-phase reaction of OH[•] radicals with β-ocimene were measured using the relative rate method over the temperature range 288–311 K at 760 Torr total pressure of nitrogen. The experiments were performed in a large volume environmental chamber using long-path FTIR spectroscopy to monitor the reactants. A room temperature rate coefficient of $k_{(\beta\text{-ocimene}+\text{OH}^\bullet)} = (2.36 \pm 0.54) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained for the title reaction. The temperature dependent rate coefficients are best fit by the Arrhenius expression $k = (4.02 \pm 0.71) \times 10^{-14} \exp(2567 \pm 211)/T$. In addition, product studies have been performed at (298 ± 2) K and 760 of Torr of synthetic air in the absence and presence of NO_x. The following molar products were determined: formaldehyde (16.5 ± 0.9)% and (24.3 ± 1.5)%, acetone (45.6 ± 2.1)% and (58.3 ± 3.4)%, methyl vinyl ketone (18.5 ± 0.8)% and <5% and glycolaldehyde (7.6 ± 0.6)% and <5% in the absence and presence of NO_x, respectively. Acetic acid (<5%) was only found in the reaction performed in the absence of NO_x. With NO_x peroxy acetyl nitrate was formed with a yield <5%. Reaction mechanisms accounting for the formation of the products are proposed and atmospheric implications are discussed.

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1. Introduction

According to emission inventories many organic compounds are emitted into the atmosphere from vegetation, whereby isoprene and monoterpenes are the main compounds.¹ β-Ocimene ((E,Z)-3,7-dimethyl-1,3,6-octatriene) is an acyclic monoterpene and emissions have been detected from plants such as wheat,² pine,³ grass land⁴ and tropical forests.⁵ In the troposphere, biogenic volatile organic compounds (BVOCs) may react with atmospheric oxidants such as OH[•] radicals, NO₃ radicals and O₃ or can be degraded by photolysis, processes that lead to the formation of a wide variety of product species and contribute to the formation of tropospheric ozone and particulate matter.⁶

The gas-phase kinetics of the OH[•] radical-initiated degradation of β-ocimene has been studied previously by Atkinson *et al.*⁷ at 294 K and by Grimsrud *et al.*⁸ at 301 K, using in both cases the relative kinetic technique. In addition, this reaction has been

studied as a function of temperature over the range 313–423 K by Kim *et al.*⁹ also using the relative kinetic technique.

Many product studies have been carried out under atmospheric conditions on the reactions of terpenes with the atmospheric oxidants (mainly with OH[•] radicals and O₃ molecules), the results of which indicate the formation of polyfunctional product compounds.^{10–13} The products of the reaction of the OH[•] radical with β-ocimene have been studied by Reissell *et al.*^{11,13} in the presence of NO. The experiments were performed in a 7900 L Teflon chamber using multiple analysis techniques, *i.e.* gas chromatography (GC) with flame ionization detection (GC-FID), GC-mass spectrometry (GC-MS) and GC-Fourier transform infrared (GC-FTIR). They observed formation of acetone and 4-methylhexa-3,5-dienal with molar yields of 18–20% and <2%, respectively. The non-observation of the co-product of acetone (4-methyl-3,5-hexadienal), was attributed to the reaction of the intermediate 1,2-hydroxyalkoxy radicals formed by OH[•] radical addition at the –CH=C(CH₃)₂ moiety in the compound with O₂ or more likely their isomerization through five- or seven-membered transition states forming multifunctional products and some acetone. The alternative explanation was that the reaction of CH₂=CH(CH₃)=CH₂C(•)HOH radicals with O₂ does not result in the formation of 4-methyl-3,5-hexadienal. These authors have also performed product studies on the reaction of OH[•] radicals with myrcene, who is structurally similar to β-ocimene. They identified acetone and the expected co-product

^aInstituto de Investigaciones en Fisicoquímica de Córdoba (I. N. F. I. Q. C.), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina. E-mail: mteruel@fcq.unc.edu.ar

^bBergische Universität Wuppertal, Fakultät für Mathematik und Naturwissenschaften, Physikalische Chemie & Theoretische Chemie, Gauss Strasse 20, 42119 Wuppertal, Germany

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4-vinyl-4-pentenal as products with higher molar yields of 36–45% and 19%, respectively.

In this work, rate coefficients for the reaction of the OH[•] radical with β-ocimene have been measured over the temperature range 288–311 K using the relative rate method. This investigation extends the previous kinetic temperature dependent study of Kim *et al.*⁹ to lower temperatures as in tropospheric environments since Kim *et al.*⁹ have reported rate coefficients as a function of temperature over the temperature range of 313–423 K.

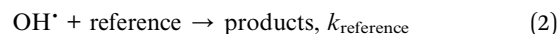
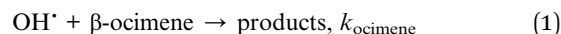
In addition, in this study we present a product distribution of the gas-phase reaction of OH[•] radicals with β-ocimene in the presence and in the absence of NO_x at 298 K and 760 Torr. To the best of our knowledge this is the first reported experimental product investigation of the OH-initiated oxidation for β-ocimene in the absence of NO_x. In contrast to the previous product studies of this reaction our investigation has been able to identify products which eluded detection in the other studies. The measured product distribution is used to propose a more comprehensive atmospheric chemical degradation mechanism for the reaction than previously possible using the older product investigations.

2. Experimental section

The experiments were performed in a 1080 L chamber over the temperature range 288–311 K in 760 Torr of nitrogen for the kinetic experiments and synthetic air for product studies. 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 reactor. Three fans with Teflon blades are mounted inside the chamber, which ensure the uniform mixing of the reactants. 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. The reactor is equipped with 32 super actinic fluorescent lamps (Philips TL 05/40 W: 320 < λ < 480 nm, λ_{max} = 360 nm) and 32 low-pressure mercury lamps (Philips TUV/40 W, λ_{max} = 254 nm) which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually. The low-pressure mercury lamps were employed for the experiments.

A white-type mirror system is mounted 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 allows “*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. Infrared spectra were recorded with a spectral resolution of 1 cm⁻¹. Typically, 60 interferograms for OH[•] reaction were co-added per spectrum and 15 such spectra were recorded per experiment. The chamber is described in greater detail in Barnes *et al.*^{14,15} The reactor is equipped with a system for temperature regulation over the range 284–313 K with a precision of ±1 K.

Rate coefficients for the reaction of OH[•] radicals with β-ocimene were determined by comparing their rate of decay with that of the corresponding decay of reference compounds:



Provided that the reference compound and the reactant are lost only by reactions (1) and (2), then it can be shown that:

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

where [ocimene]_o, [reference]_o, [ocimene]_t and [reference]_t are the concentrations of the compound studied and reference compound at times *t* = 0 and *t*, respectively, *k*_{ocimene} and *k*_{reference} are the rate coefficients of reactions (1) and (2), respectively.

Hydroxyl radicals were generated from the 254 nm photolysis of hydrogen peroxide (H₂O₂). The relative rate technique relies on the assumption that the β-ocimene and reference compound are removed solely by reaction with the OH[•] radicals. To verify this assumption, the concentrations of β-ocimene and the reference compounds were monitored, in the absence of H₂O₂, in the dark and also with the photolysis lamps switched on for time periods equivalent to those used for the experiments. No significant changes of the β-ocimene and reference compound concentrations were observed. 2,3-Dimethyl-2-butene with a rate coefficient of *k*_{OH} = (1.09 ± 0.04) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (ref. 16) was used as a reference compound for the determination of the rate coefficient of OH[•] with β-ocimene at 298 K. Isobutene was employed as reference compound for the temperature dependent studies using the Arrhenius expression *k* = 0.947 × 10⁻¹¹ exp(504/*T*⁻¹) cm³ molecule⁻¹ s⁻¹ to calculate the rate coefficients for the appropriate temperature.^{6,17}

To identify and to quantify the products formed in the reaction of OH[•] radical with β-ocimene, mixtures of H₂O₂/β-ocimene/air (with and without NO) were irradiated for periods of 16–20 min during the course of which infrared spectra were recorded with the FTIR spectrometer. Typically 60 interferograms were co-added per spectrum over a period of approximately 1 min and 20 such spectra were collected.

Reactants and products were quantified by comparison with calibrated reference spectra contained in the IR spectral databases of the laboratory in Wuppertal. The reactants were monitored at the following infrared absorption frequencies (in cm⁻¹): β-ocimene 2700–3150; 2,3-dimethyl-2-butene 2800–3050; isobutene 890. The products observed were monitored at the following infrared spectra (in cm⁻¹): acetone 1217; methyl vinyl ketone 952; glycolaldehyde 1764; formaldehyde 2766; acetic acid 1184 and peroxy acetyl nitrate 1163.

The initial concentrations of the organic compounds (1 ppmV = 2.46 × 10¹³ molecule cm⁻³ at 298 K) were: 2.7–3 ppmV for β-ocimene; 2.3–2.6 ppmV for 2,3-dimethyl-2-butene; 1.9–2 ppmV for isobutene; ~7 ppmV for H₂O₂ and 3 ppmV for NO. 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%), nitric oxide (Messer Griesheim, 99.5%), hydrogen peroxide (Peroxid-Chemie GmbH, 85%), β -ocimene mixture of *cis/trans* isomers (Aldrich, $\geq 90\%$), 2,3-dimethyl-2-butene (Aldrich, 98%) and isobutene (Messer Griesheim, 99%).

3. Results and discussion

3.1. Room temperature rate coefficient

Fig. 1 shows the kinetic data, plotted according to eqn (I), obtained from experiments on the reaction of the OH \cdot radical with β -ocimene at 298 K measured relative to the reference compounds 2,3-dimethyl-2-butene and isobutene. Each plot represents three experiments for each reference compound and as can be seen linear relationships were obtained for both reference compounds. Listed in Table 1 are the rate coefficient ratios $k_{\text{ocimene}}/k_{\text{reference}}$ obtained from the kinetic plots and the corresponding rate coefficients for the reaction of OH \cdot with β -ocimene put on an absolute basis using the rate coefficient values of the reference compound given in the Experimental section. Since all the rate coefficient values obtained for the reaction of OH \cdot with β -ocimene from the individual experiments using two reference compounds are in excellent

agreement we prefer to quote a final value for the rate coefficient which is the average of all the determined values. This results in the following final averaged value for the reaction at 298 K:

$$k_{(\beta\text{-ocimene}+\text{OH}\cdot)} = (2.36 \pm 0.54) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The above value for the reaction of OH \cdot with β -ocimene measured in this work at 298 K can be compared with other reported literature values. Kim *et al.*⁹ have reported a value of $(3.03_{-0.39}^{+0.44}) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction at 298 K measured relative to OH \cdot with isobutene. They performed the investigations in a 160 cm³ quartz reaction chamber using GC-MS for the analysis. The value of the rate coefficient at 298 K quoted by the authors is derived from their Arrhenius expression. Atkinson *et al.*⁷ report a value of $(2.50 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction at 294 K measured relative to 2,3-dimethyl-2-butene. Their study was carried out in 6400 L all-Teflon chamber using CG/FID for the analysis. Finally, Grimsrud *et al.*⁸ report a value of $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction at 301 K measured relative to isobutene. The value of the rate coefficient obtained in this work for the reaction at 298 K of $(2.36 \pm 0.54) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in excellent agreement with the value reported by Atkinson *et al.*⁷ and agrees within the reported error limits with that reported by Kim *et al.*⁹ Our value is 36% lower than the value of $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Grimsrud *et al.*⁸

Linear free-energy relationships are often used to estimate rate coefficients for the reactions of compounds with atmospheric oxidants which have not yet been the subject of experimental determination. These correlations are based on the assumption that the electrophilic addition of oxidants such as OH \cdot radicals, O(³P) atoms, NO₃ radicals, O₃ molecules and Cl atoms to unsaturated compounds proceed *via* similar reaction mechanisms and, therefore, the rate coefficients for the reactions should be well correlated with one another.^{18–21} In this work, we present the correlation between k_{OH} and k_{O_3} for a series of acyclic alkenes and terpenes containing a conjugated double bond moiety. Table 2 lists the recommended room temperature rate coefficients for the reactions of different alkenes and terpenes with OH \cdot radicals and O₃ molecules. Fig. 2 shows a plot of the log k_{O_3} values *versus* the corresponding log k_{OH} values. As seen in Fig. 2 a reasonable correlation is obtained. A least-squares treatment of the data ($r^2 = 0.89$) yields the following expression (rate coefficients in units of cm³ molecule⁻¹ s⁻¹):

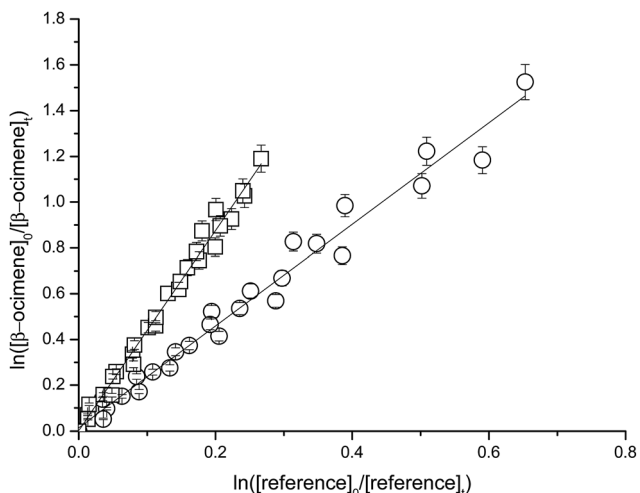


Fig. 1 Plot of the kinetic data for the reaction of the OH \cdot radical with β -ocimene measured relative to (O) 2,3-dimethyl-2-butene and (□) isobutene at 298 \pm 2 K and atmospheric pressure of N₂.

Table 1 Rate coefficient ratios $k_{\text{ocimene}}/k_{\text{reference}}$ and absolute rate coefficients for the reaction of the OH \cdot radical with β -ocimene at 298 K in (760 \pm 10) Torr of nitrogen

Reaction	Reference	$k_{\text{ocimene}}/k_{\text{reference}}$	$k_{\text{ocimene}} \times 10^{10} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}$
β -Ocimene + OH \cdot	2,3-Dimethyl-2-butene	2.038 ± 0.039	2.22 ± 0.13
	2,3-Dimethyl-2-butene	2.333 ± 0.058	2.54 ± 0.16
	2,3-Dimethyl-2-butene	2.335 ± 0.054	2.55 ± 0.16
	Isobutene	4.753 ± 0.105	2.44 ± 0.54
	Isobutene	4.253 ± 0.084	2.19 ± 0.48
	Isobutene	4.316 ± 0.066	2.22 ± 0.48
	Average:		2.36 ± 0.54

Table 2 Room temperature rate coefficients for the reactions of OH[•] radicals and O₃ molecules with a series of acyclic alkenes and terpenes with a conjugated double bond system

Row	Compounds	$k_{\text{OH}^\bullet} \times 10^{10}$ (cm ⁻³ molecule ⁻¹ s ⁻¹)	$k_{\text{O}_3} \times 10^{17}$ (cm ⁻³ molecule ⁻¹ s ⁻¹)
1	CH ₂ =CHCH=CH ₂ 1,3-butadiene	0.666 (ref. 36)	0.624 (ref. 36)
2	CH ₂ =C(CH ₃)C(CH ₃)=CH ₂ 2,3-dimethyl-1,3-butadiene	1.25 (ref. 36)	2.62 (ref. 36)
3	CH ₂ =CHCH=CHCH ₃ 1,3-pentadiene	1.03 (ref. 36)	2.78 (ref. 36)
4	CH ₂ =CHCH=CHCH=CH ₂ 1,3,5-hexatriene	1.04 (ref. 36)	2.62 (ref. 36)
5	CH ₂ =C(CH ₃)CH=CH ₂ isoprene	1.11 (ref. 36)	1.30 (ref. 36)
6	CH ₃ C(CH ₃)=CHCH ₂ CH=C(CH ₃)CH=CH ₂ β-ocimene	2.36 (this work)	38.5 (ref. 9)
7	CH ₂ C(CH ₃)=CHCH ₂ CH ₂ C(=CH ₂)CH=CH ₂ β-myrcene	3.35 (ref. 9)	38.5 (ref. 9)
8	CH ₂ =CHC(=CH ₂)CH ₂ CH ₂ CH=C(CH ₃)CH ₂ CH ₂ CH=C(CH ₃)CH ₃ β-farnesene	2.88 (ref. 9)	68.6 (ref. 9)
9	CH ₂ =CHC(CH ₃)=CHCH ₂ CH=C(CH ₃)CH ₂ CH ₂ CH=C(CH ₃)CH ₃ α-farnesene	2.19 (ref. 9)	59.4 (ref. 9)

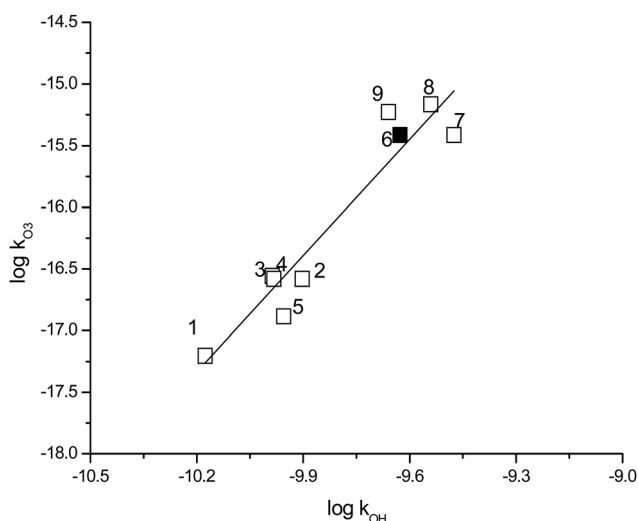


Fig. 2 Linear free energy plot of $\log k_{\text{O}_3}$ against $\log k_{\text{OH}^\bullet}$ at room temperature for a series of acyclic alkenes and terpenes with a conjugated double bond system. See Table 2 for the number interpretations.

$$\log k_{\text{O}_3} = (3.15 \pm 0.38) \log k_{\text{OH}^\bullet} + (14.75 \pm 3.75)$$

The good correlation supports that the mechanism of the reactions of the OH[•] radical with the selected acyclic polyalkenes and terpenes is similar to that for the reactions of the compounds with O₃ molecules, *i.e.* the addition of OH[•] or O₃ to the double bonds of the unsaturated compounds in a reversible step forming an adduct, which can react in subsequent fast reactions forming products.^{7,17} Using the correlation obtained in this work, reasonably precise estimations can be made of rate coefficients for reactions of OH[•] or O₃ with acyclic polyunsaturated compounds which have not yet been determined experimentally.

3.2. Dependence of the rate coefficient on temperature

The temperature dependence of the reaction of OH[•] radical with β-ocimene was studied over the temperature range 288–311 K using isobutene as the reference compound. Fig. 3 shows the

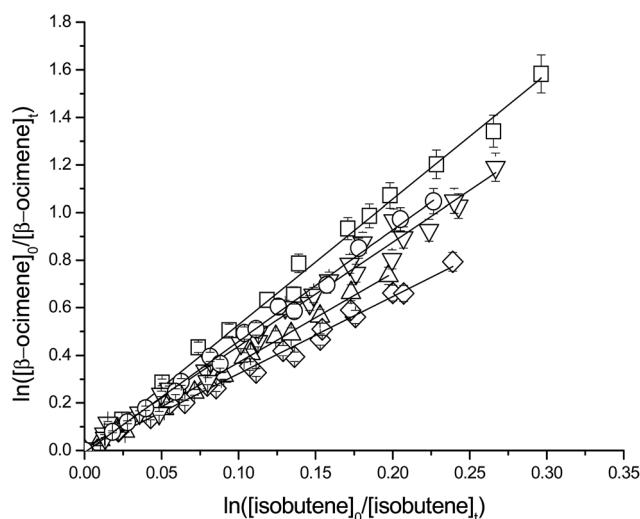


Fig. 3 Plot of the kinetic data for the reaction of the OH[•] radical with β-ocimene measured relative to isobutene in an atmosphere of N₂ over the temperature range 288–311 K: 288 K (□), 293 K (○), 298 K (▽), 303 K (Δ) and 311 K (◇).

kinetic data obtained from the experiments performed at 288, 293, 298, 303 and 311 K plotted according to eqn (I). Good linear correlations were obtained at all temperatures. The rate coefficients for the reaction of OH[•] with β-ocimene, derived from linear least-squares analysis of each experimental data set at the individual temperatures investigated, are listed in Table 3. The errors quoted for the rate coefficients are twice the standard deviation arising from the straight line least-squares fits of the data, plus an additional 20% to take into account uncertainties in the rate coefficient for isobutene. An Arrhenius plot of the kinetic data is shown in Fig. 4. The following Arrhenius expression has been derived from a linear least-squares treatment of the plot:

$$k(\text{OH}^\bullet + \beta\text{-ocimene}) = (4.02 \pm 0.71) \times 10^{-14} \exp((2567 \pm 211)/T)$$

The rate coefficients for the reaction of OH[•] with β-ocimene were found to decrease with increasing temperature over the

Table 3 Rate coefficients and Arrhenius parameters for the reactions of the OH[•] radical with β-ocimene over the temperature range 288–311 K measured in 760 ± 10 Torr of nitrogen

Reaction	Temperature	$k_{\text{ocimene}} \times 10^{10}$ (cm ³ molecule ⁻¹ s ⁻¹)	-Ea/R (K)	A × 10 ¹⁴ (cm ³ molecule ⁻¹ s ⁻¹)
β-Ocimene + OH [•]	288 K	2.95 ± 0.68	2567 ± 211	4.02 ± 0.71
	293 K	2.53 ± 0.56		
	298 K	2.36 ± 0.54		
	303 K	1.87 ± 0.44		
	311 K	1.54 ± 0.36		

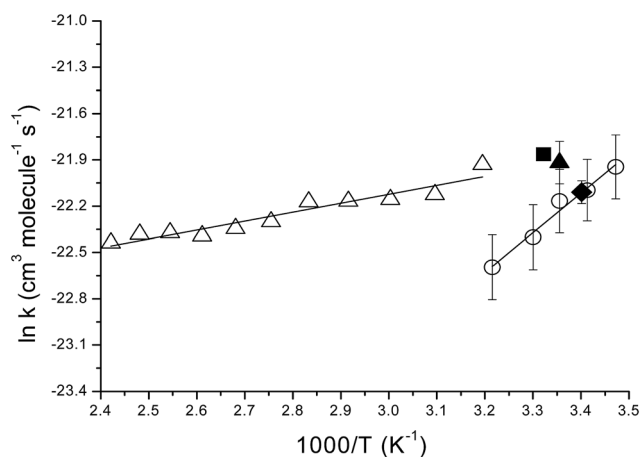


Fig. 4 Arrhenius plot of the kinetic data for the reaction of the OH[•] radical with β-ocimene over the temperature range 288–311 K. The data obtained in this work is compared with the Arrhenius plot obtained by Kim *et al.* (2011) over the temperature range of 313–413 K (Δ) and the literature values of the rate coefficients at 301 K obtained by Grimsrud *et al.* (1975) (■), at 294 K obtained by Atkinson *et al.* (1986) (◆) and at 298 K from the Arrhenius expression obtained by Kim *et al.* (2011) (▲).

temperature range 288–311 K. Kim *et al.*⁹ also observe negative temperature dependence for the reaction and this is plotted in Fig. 4 together with the other two room temperature values of the rate coefficient obtained by Grimsrud *et al.*⁸ and Atkinson *et al.*⁷ The negative temperature of the reaction observed in this work is much stronger than that observed by Kim *et al.*⁹ our value of Ea/R is a factor of 4 higher than their value for the reaction.

The negative temperature dependence of the reaction of OH[•] with β-ocimene can be justified on a qualitative basis assuming that the lifetime of the excited bimolecular complex, formed between the OH[•] radical and the terpene, with respect to decomposition back to the reactants decreases as the temperature increases. The probability of the excited adduct being stabilized by collision with a third body decreases with increasing temperature. Alternately, one can treat a termolecular reaction as the sum of individual bimolecular reactions, which result in an effective activation energy for the global reaction, *i.e.* the overall activation energy is the sum of the energies for the individual steps. The effective activation energy for the reaction is negative and the rate coefficient decreases as the temperature increases when the activation energy for the

energized complex back to reactants is greater than the sum of those for its formation and reactions to form products.²²

3.3. Product studies

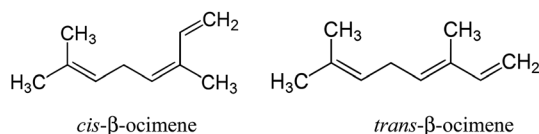
3.3.1 Observed products. Panel A in Fig. S1 (see ESI†) shows the infrared spectrum of a β-ocimene/H₂O₂/air reaction mixture after irradiation and subtraction of residual β-ocimene. Panels B, C, D, E and F show reference spectra of acetone, methyl vinyl ketone, formaldehyde, glycolaldehyde and acetic acid, respectively. Panel G shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A. In Fig. S2,† panel A shows the infrared spectrum of a β-ocimene/H₂O₂/NO/air reaction mixture after irradiation and subtraction of residual β-ocimene. Panels B, C, D, E and F show reference spectra of acetone, methyl vinyl ketone, formaldehyde, glycolaldehyde and peroxy acetyl nitrate, respectively. Panel G shows the residual product spectrum obtained after subtraction of features due to acetone, methyl vinyl ketone, formaldehyde, glycolaldehyde and acetic acid from the spectrum in panel A.

Formation of acetone, methyl vinyl ketone, formaldehyde, glycolaldehyde and acetic acid was observed in the experiments performed in the absence of NO and acetone, methyl vinyl ketone, formaldehyde, glycolaldehyde and peroxy acetyl nitrate was observed in the experiments performed in the presence of NO_x. Concentration–time profiles of β-ocimene and the identified products in the absence and presence of NO are presented in Fig. S3 and S4,† respectively. The concentration–time profiles support that acetone, methyl vinyl ketone, glycolaldehyde, formaldehyde and acetic acid are to a large extent primary products in the absence of NO and acetone, methyl vinyl ketone, glycolaldehyde, formaldehyde and peroxy acetyl nitrate are to a large extent primary products in presence of NO. This linearity does not, however, exclude contributions to some of the products from secondary reactions.

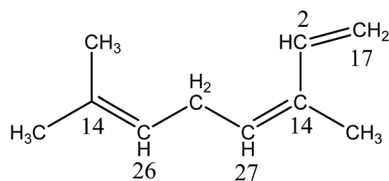
Plots of the concentrations of acetone, methyl vinyl ketone, formaldehyde, glycolaldehyde and acetic acid, as a function of consumed β-ocimene all show reasonable linearity. Such plots for the products formed in the OH[•] + β-ocimene reaction in the absence of NO are shown in Fig. S5† and the corresponding plots for the products formed in the presence of NO in Fig. S6.† The reactions of OH[•] with formaldehyde, methyl vinyl ketone and glycolaldehyde have IUPAC²³ recommended 298 K rate coefficients values (in cm³ molecule⁻¹ s⁻¹) of 8.5×10^{-12} , 2.0×10^{-11} and 8.0×10^{-12} , respectively. Formaldehyde, methyl vinyl

ketone and glycolaldehyde will be subject to secondary consumption by OH[•] in the reaction system. To estimate the extent of secondary consumption by OH[•] for these compounds the formation yield correction method outlined in Tuazón *et al.*²⁴ was used. The calculated secondary consumption in the reaction system for these carbonyl compounds was less than 1% in all cases and has, therefore, not been taken into consideration in the reported formation yields. The formation yields of the oxidation products identified in the OH[•]-radical initiated oxidation of β-ocimene in the presence and absence of NO are listed in Table 4.

The sample of β-ocimene investigated was a racemic mixture of the *cis* and *trans* isomers the chemical structures of which are shown below:



The molecular structure of β-ocimene contains isobutene ((CH₃)₂C=C-) and isoprene (-CH=C(CH₃)-CH=CH₂) type moieties. The reaction of OH[•] radicals with β-ocimene proceeds overwhelmingly by addition of OH[•] to the three double bonds in the molecule to form hydroxyalkyl radicals, which react rapidly under the experimental conditions with oxygen to form hydroxy peroxy radicals. The structure-reactivity relationship of Kwok and Atkinson²⁵ predicts that ~62% of the OH[•] addition will occur at the -CH=C(CH₃)-CH=CH₂ moiety and ~38% at the (CH₃)₂C=CH- moiety with a negligible contribution from H-atom abstraction pathways. The SAR of Peeters *et al.*²⁶ for (poly)alkenes not only predicts a similar OH[•] addition percentage for the two double bond moieties but also gives estimations of the site-specific contributions of OH[•] addition to the double bonds. The OH[•]-radical site specific addition estimates, as percentages of the overall rate coefficient, are shown below:



Addition of OH[•] at the isobutene moiety will lead to formation of two 1,2-hydroxy peroxy radicals. Due to resonance between the two double bond units in the isoprene moiety in β-ocimene formation of six different hydroxyperoxy radicals is possible, *i.e.* four 1,2-hydroxyperoxy and two 1,4-hydroxyperoxy radicals which can have E and Z configurations.

In the presence of NO, at the levels used in the experiments, the hydroxyperoxy radicals will be mainly converted to hydroxyalkoxy radicals, however, formation of hydroxynitrates is also possible. In absence of NO the hydroxyperoxy radicals will undergo self-reactions or reactions with other peroxy radicals (HO₂/RO₂) to form a large extend hydroxyalkoxy radicals, although molecular channels are also possible.^{27,28} Reactions of the hydroxyperoxy radicals with HO₂ radicals could potentially lead to the formation of hydroxy-hydroperoxides. At the radical levels present in the experiments it is very unlikely that isomerization of the hydroxyl peroxy radicals, as reported for the reaction of OH[•] with isoprene,²⁹ will occur. The hydroxyalkoxy radicals can react further with molecular oxygen or decompose by C-C scissions. In the case of β-ocimene, isomerization can also occur through five or six membered transition states, leading to the formation of multifunctional products that will still contain >C=C< moieties.¹³

In this study, the yields of acetone obtained in the absence and presence of NO_x are (45.6 ± 2.1)% and (58.3 ± 3.4)%, respectively. The main route to the formation of acetone is attributed to decomposition of the CH₂=CHC(CH₃)=CHCH₂-CH(OH)C(O[•])(CH₃)CH₃ and CH₂=CHC(CH₃)=CHCH₂CH(O[•])C(OH)(CH₃)CH₃ radicals. These radicals are generated by addition of the OH radical to the double bond between C₆ and C₇ (see channel A₁ and channel A₂ in Fig. S7[†]). The yields of acetone are ~8% and ~20% higher, for the absence and presence of NO_x, respectively, than the ~38% estimated fraction of the overall OH[•] radical reaction performing by initial OH[•]-radical addition to the -CH=C(CH₃)₂ moiety. Tuazón *et al.*³⁰ have observed high yields of acetone in their study on the reaction of OH radicals with 2-methylpropene, 2-methyl-2-butene and 2,3-dimethyl-2-butene in the presence of NO_x. Each of these alkene contains an >C=C entity and Tuazón *et al.*³⁰ found that for each alkene bond cleavage of the intermediate hydroxyalkoxy radicals to form acetone in yields of ~90% dominated over reaction of the radicals with O₂. The high yields of acetone observed in this study for the reaction OH[•] with β-ocimene support that the main fate of the hydroxyalkoxy radicals formed by addition of the OH[•] radical to the double

Table 4 Formation yields of the oxidation products identified in the OH[•]-radical oxidation of ocimene studied in both the presence and absence of NO at 298 K and 760 ± 10 Torr of air

Reaction	Product	Yield (%) (3 ppmV NO _x)	Yield (%) (NO _x -free)
β-Ocimene + OH [•]	HC(OH) formaldehyde	24.3 ± 1.5	16.5 ± 0.9
	CH ₃ C(O)CH ₃ acetone	58.3 ± 3.4	45.6 ± 2.1
	CH ₃ C(O)CH=CH ₂ methyl vinyl ketone	<5%	18.5 ± 0.8
	HOCH ₂ C(O)H glycolaldehyde	<5%	7.6 ± 0.6
	CH ₃ C(O)OONO ₂ peroxy acetyl nitrate (PAN)	<5%	—
	CH ₃ C(O)OH acetic acid	—	<5%

bond between C₆ and C₇ will also be bond cleavage to form acetone and that the alternative reaction pathways of the radicals with O₂ and possibly also isomerization are insignificant.

It is quite probable that there is some secondary formation of acetone in the reaction systems through reactions of OH[•] with reaction products that contain the >C=C entity. In Fig. S6,† although a straight line has been drawn through the measurements points to obtain the yield, closer inspection of the last 4 points in the plot suggest that some upward curvature is occurring, which would be indicative of secondary acetone formation. Secondary formation of acetone could explain the much higher yield of acetone observed in the presence of NO_x compared to that in its absence where the yield is more in accord with the calculated fraction of the reaction proceeding *via* OH[•] radical addition to the >C=C entity. A comparison of the ocimene decay in Fig. S3 and S4† shows that the decay of ocimene is much faster in the presence of NO_x due to the higher levels of OH[•] which are generated by the NO_x chemistry in the system thus causing a faster ocimene decay and consequently more secondary formation of acetone.

Reissell *et al.*^{11,13} have determined the yield of acetone in the OH[•]-radical initiated oxidation of ocimene in the presence of NO at room temperature and 740 Torr total pressure of air in large Teflon chambers using GG/FID and CG/MS to detect acetone. In these studies they report acetone molar formation yields of only 18% and 20%. The yield of acetone in the presence of NO_x obtained in this work is a factor of ~3 higher than the yields reported by Reissell *et al.*^{11,13} Curiously, Reissell *et al.*¹³ report a yield of 45% for acetone formation in the OH[•]-radical initiated oxidation of the structurally similar myrcene. Reissell *et al.*¹³ offer various explanations for the much lower acetone yield they observe in the reaction of OH[•] with ocimene compared to myrcene, however, we have performed extensive compound calibration and spectra subtraction checks to confirm our yields and suspect that the low acetone yields obtained by Reissell *et al.*^{11,13} has other, as yet unknown, reasons. Reissell *et al.*¹¹ report that ocimene reacts in the dark with NO₂, however, inspection of the dark period in our product study on the reaction of OH[•] with ocimene in the presence of NO_x (see Fig. S4†) shows that under our conditions reaction of ocimene with NO₂ was negligible. Based on the results of Reissell *et al.*¹¹ any significant interference by reaction of NO₂ with ocimene in our experimental system would have caused a decrease in the acetone yield over the NO_x-free case rather than the significant enhancement which we observe.

Formaldehyde has been identified and quantified with a yield of (24.3 ± 1.5)% in the presence of NO_x and (16.5 ± 0.9)% in absence of NO_x. According to the mechanisms presented in Fig. S7–S9,† formaldehyde could be formed by decomposition

of the radicals CH₂=CHC(CH₃)=CHCH₂CH(OH)C(O[•])(CH₃)CH₃, [•]OCH₂CH(OH)C(CH₃)=CHCH₂CH=C(CH₃)CH₃ and CH₂=CHC(O[•])(CH₃)CH(OH)CH₂CH=C(CH₃)CH₃ generated by addition of the OH radical at C₆, C₁ and C₄, respectively (see channel A₂ in Fig. S7,† channel A₁ in S8 and channel A₂ in S9). No other yield for the formation of formaldehyde from the reaction of β-ocimene + OH[•] has been reported in the literature. However, a yield of (30 ± 6)% has been reported for formaldehyde formation in the reaction of OH[•] with myrcene by Orlando *et al.*,¹² which it is structurally similar to β-ocimene, they performed their study in the presence of NO_x in a stainless steel environmental chamber using long-path FTIR for the analysis. Taking into account the structural similarity between of β-ocimene and myrcene and consequently, the similarity in the degradation pathways with OH[•] radicals, the yield of formaldehyde obtained in this work in the presence of NO_x is in relatively good agreement with the value obtained by Orlando *et al.*¹²

Glycolaldehyde was formed with a yield of (7.6 ± 0.6)% in the absence of NO_x and <5% in the presence of NO_x. We suggest that this product is formed by decomposition of the HOCH₂-CH(O[•])C(CH₃)=CHCH₂CH=C(CH₃)CH₃ radical which results when the OH[•] radical adds to the C₁ position (see channel B₁ in Fig. S8†). Formation of methyl vinyl ketone has been observed with yields of (18.5 ± 0.8)% in the absence of NO_x and <5% in the presence of NO_x. This product is probably formed according to the mechanism shown in Fig. S9,†*i.e.* through decomposition of the CH₂=CHC(O[•])(CH₃)CH(OH)CH₂CH=C(CH₃)CH₃ radical formed by the addition of the OH[•] radical to the C₄ position (see channel A₁ Fig. S9†). In addition, formation of acetic acid was observed in the absence of NO_x with a yield of <5%, and it is suggested that it is formed by decomposition of the CH₃-CH(O[•])(OH)CH=CH₂ radical. This radical is generated by the decomposition of the hydroxyalkoxy radical formed by channel B₁ shown in Fig. S9.† Formation of acetic acid was not observed in experiments carried out in the presence of NO_x.

The results obtained in this study indicate that acetone is a major product of the OH[•]-radical initiated degradation of β-ocimene both in the absence and presence of NO_x. Therefore, the addition of the OH[•] radical to the double bond between C₆ and C₇ and the following decomposition of the intermediate hydroxyalkoxy radicals (see channel A₁ and B₁ in Fig. S7†) are the main degradation pathways for the studied reaction both in the presence and the absence of NO_x. The formation of methyl vinyl ketone is more favored in the absence of NO_x. This is contrary to expectations since one would expect that the formation of the hydroxyalkoxy radical, which leads to formation of the ketone (channel A in Fig. S9†), would be more efficiently generated in the presence of NO. The hydroxyalkoxy

Table 5 Atmospheric lifetimes of β-ocimene with respect to their reactions with O₃, OH[•] and NO₃

Compound	$k_{\text{OH}} \times 10^{10}$ (cm ³ molecule ⁻¹ s ⁻¹)	τ_{OH} (min)	$k_{\text{O}_3} \times 10^{16}$ (cm ³ molecule ⁻¹ s ⁻¹)	τ_{O_3} (min)	$k_{\text{NO}_3} \times 10^{11}$ (cm ³ molecule ⁻¹ s ⁻¹)	τ_{NO_3} (min)
β-Ocimene	2.36 (this work)	35	3.85 (ref. 9)	62	2.40 (ref. 38)	1
	2.50 (ref. 7)	33	5.60 (ref. 37)	43		

radical generated in the presence of NO will be chemically activated and it would appear that this may cause the radical to react by other pathways such as decomposition or isomerization leading to the formation of an oxygenated compound other than methyl vinyl ketone. Also the formation of glycolaldehyde is slightly favored in the absence of NO_x over the presence of NO_x, the difference, however, is not very significant.

The formation of 4-methyl-3,5-hexadienal, methyl-vinyl-ketone and acetone have been observed as major oxidation products during sunlight irradiation of ocimene/NO_x mixtures^{31,32} which will involve both OH[•]- and O₃-mediated oxidation of ocimene. Unfortunately we have no information on product yields from the studies. Besides formaldehyde, methylglyoxal and malonaldehyde three higher aldehydes were also tentatively identified in small amounts.

3.3.2 Atmospheric implications. Calculated tropospheric lifetimes of β-ocimene with respect to reaction with OH[•] radicals, O₃ molecules and NO₃ radicals are given in Table 5. These lifetimes have been calculated using the expression: $\tau_x = 1/k_x[X]$ with X = OH[•], O₃ or NO₃, where 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. The following typical oxidant concentrations have been used: [OH[•]] = 2 × 10⁶ radical cm³,³³ [O₃] = 7 × 10¹¹ molecule cm³ (ref. 34) and [NO₃] = 5 × 10⁸ radical cm³.³⁵ Photolytic loss of β-ocimene is not relevant in the troposphere since it does not absorb in the actinic region. Similarly, wet and dry depositions are expected to be of minor importance due to the short lifetime of β-ocimene in the atmosphere. The calculated lifetimes for reaction of β-ocimene with the oxidants OH[•] and NO₃ radicals and O₃ indicate that it will be rapidly degraded in the troposphere and thus contribute to secondary pollutant formation close to its emission source. The nighttime NO₃ radical and the daytime OH[•] radical reactions dominate the loss processes, however, in moderately polluted areas reaction with O₃ molecules will also play a role. The work has shown that the reaction of OH[•] with β-ocimene is an important source of acetone and several other oxygenated compounds which still need to be identified. The work indicates that reaction of some of these oxygenate compounds will also react with OH[•] to form acetone.

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