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Atmospheric sink of β-ocimene and camphene initiated by Cl atoms: kinetics and products at NOx free-air†

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Rate coefficients for the gas-phase reactions of Cl atoms with β-ocimene and camphene were determined to be (in units of 10^{-10} cm^3 per molecule per s) 5.5 ± 0.7 and 3.3 ± 0.4, respectively. The experiments were performed by the relative technique in an environmental chamber with FTIR detection of the reactants at 298 K and 760 torr. Product identification experiments were carried out by gas chromatography with mass spectrometry detection (GC-MS) using the solid-phase microextraction (SPME) method employing on-fiber carbonyl compound derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride. An analysis of the available rates of addition of Cl atoms and OH radicals to the double bond of alkenes and cyclic and acyclic terpenes with a conjugated double bond at 298 K is presented. The atmospheric persistence of these compounds was calculated taking into account the measured rate coefficients. In addition, tropospheric chemical mechanisms for the title reactions are postulated.

1. Introduction

The interaction between the biosphere and atmosphere is essential for all living systems and organisms. Hundreds of Volatile Organic Compounds (VOCs) are released from biogenic sources. The first biogenic volatile organic compound (BVOC) specifically identified to be important for atmospheric composition was isoprene.[1] The biogenic VOCs include isoprenoids (isoprene and terpenes), alkanes, alkenes, carbonyls, alcohols, esters, ethers and acids, where the predominant species is isoprene. VOCs emitted from biogenic sources are more reactive than VOCs with anthropogenic origin.[2]

Atmospheric concentrations of BVOCs range from few ppt to several ppb and their reactivity is high as reflected by their chemical lifetimes which range from minutes to hours.[1] Many species of biogenic VOCs are rapidly oxidized by O_3, OH radicals and/or NO_3 radicals and it is also possible through reaction with chlorine (Cl) atoms. This later reaction has generally only been considered to be of importance in coastal and marine air environments.[3-8] However, in field studies evidence has been

presented for Cl chemistry in continental regions far removed from coastal and marine regions where observations of nitryl chloride ($ClNO_2$), a gaseous photolytic Cl atom precursor, were made[9-12] and in a recent study, different chlorine species have been detected in particles in urban air.[13]

Atmospheric degradation of BVOCs leads to the production of secondary chemical species which can enhance concentrations of tropospheric ozone and other oxidants in areas rich in nitrogen oxides and monoterpenes.[2] On the other hand, the oxidation of BVOCs under low concentrations of NO_x generates peroxides and acids.[14] Acids as well as some other BVOC oxidation products may undergo gas-to-particle conversion leading to the growth of secondary organic aerosols (SOA).[15]

Monoterpene compounds as β-ocimene and camphene are emitted especially by conifers such as pine, spruce, fir, mint or citrus families[16-18] and are known to constitute the main fraction of terpenic or essential oils produced in plant secretory organs.[1] Monoterpene emissions are mostly dependent on ambient temperature, which typically increases their emissions. Some species (*e.g.* oaks) also show light-dependence of emissions suggesting link between monoterpene formation and photosynthetic process. Therefore, weather extreme conditions (such as high temperature) have large implications for the fluxes of matter between plants and the atmosphere that will also impact on the atmospheric chemistry.[19,20]

In order to assess the impact of these species on air quality, kinetic and mechanistic information on their tropospheric degradation is therefore needed.

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In this work, we report room temperature relative kinetic determinations of the rate coefficients for the reactions of Cl atoms with β-ocimene and camphene performed in a long path photoreactor coupled to an FTIR spectrometer at room temperature and atmospheric pressure of nitrogen:
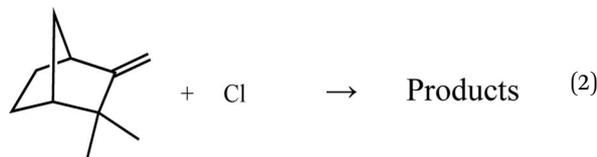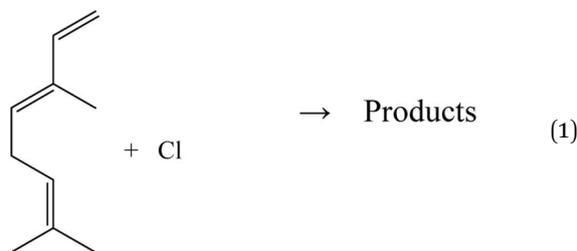
To the best of our knowledge, this work provides the first kinetic and product study for the reactions of Cl atoms with both monoterpenes. The aim of this study was to extend our earlier work on the reactivity of these monoterpenes toward OH radicals and O_3 molecules.[21–23] Kinetic data for these Cl reactions are needed to facilitate a better understanding of the oxidation mechanisms of these monoterpenes so that their role in tropospheric atmospheric chemistry can be better assessed. The measurements will also help to develop a more reliable structure–reactivity relationship for these biogenic compounds. Moreover, it has been identified reaction products due to the degradations of the studied monoterpenes with Cl atoms.

In addition to the kinetic experimental investigations, a correlation between the rate coefficients for the reactions of OH radicals with the monoterpenes studied in this work together with other monoterpenes and alkenes and those for the corresponding reactions with Cl atoms has been examined.

The atmospheric lifetimes of the BVOCs studied, with respect to reaction with Cl atoms, have been calculated with the rate coefficients obtained in this work and compared with the lifetimes of β-ocimene and camphene due to other homogeneous sinks in the troposphere. Products of the studied reactions has been identified using solid-phase microextraction (SPME) technique employing on-fiber carbonyl compound derivatization with detection system gas chromatograph-mass spectrometer (GC-MS).

2. Experimental

All the experiments were performed in a 1080 dm^3 quartz–glass reaction chamber at a total pressure of 760 torr (760 torr = 101.325 kPa) and 298 ± 3 K in nitrogen. A detailed description of the reactor can be found elsewhere[24] and only a brief description is provided here. A pumping system consisting of a turbo-molecular pump backed by a double-stage rotary fore pump

was used to evacuate the reactor to 10^{-3} torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 low-pressure mercury lamps (Philips TUV 40 W, $\lambda_{max} = 254$ nm), spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, allowing a variation of the light intensity, and thus the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive *in situ* long path absorption monitoring of reactants and products in the IR spectral range 4000–700 cm^{-1}. The White system was operated at 82 traverses, giving a total optical path length of (484.7 ± 0.8) m. The IR spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FT-IR spectrometer, equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. For the reaction of β-ocimene + Cl, 60 interferograms were co-added and for the reaction of camphene + Cl, 80 interferograms were co-added, for both reactions 20 spectra were recorded per experiment.

Chlorine atoms were generated by the photolysis of oxalyl chloride with the germicidal lamps

$$ClC(O)C(O)Cl + h\nu \rightarrow 2Cl + 2CO \qquad (3)$$

The initial concentrations of reactants in ppmV (1 ppmV = 2.46×10^{13} molecule per cm^3 at 298 K) were: β-ocimene, (2.1–2.7); camphene, (1.7–2.2); oxalyl chloride, (1.4–2.0); isobutene, (1.8–2.0) and propene, (3.7–4).

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): β-ocimene at 2700–3150; camphene at 882; isobutene at 890 and propene at 912.

Room temperature products identification experiments were carry out using SPME (grey fiber, PDMS/CAR/DVB, SUPELCO)/ GC-MS (Varian CP3800) technique. Mixture of β-ocimene/ ClC(O)C(O)Cl/air and camphene/ClC(O)C(O)Cl/air were flushed into the Teflon bag, respectively. The photolysis time was 10 s for each experiment, it was a experimentally considerable time in which the reactants have not been completely consumed with appreciable formation of the reaction products. In order to identify carbonyl products a 2 mL aqueous solution of *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) of 25 mg mL^{-1} was used as derivatizing agent. The PFBHA reacts with carbonyl compounds forming a stable oxime. The PFBHA was loaded on the SPME fiber during 1 min by head-space extraction. The fiber-PFBHA was exposed during 2 min for the β-ocimene–Cl reaction and 3 min for camphene–Cl reaction inside the chamber to produce the oxime on the fiber to be transferred to the GC-MS injector. The desorption time was 3 min at 200 °C. It was employed a capillary column HP-5MS (30 m × 0.250 mm, film 0.25 μm Agilent Part N 19091S-433). The temperature program was 80 °C for 3 min, 100 °C for 5 min, 200 °C for 5 min to 250 °C at a rate of 15 °C min^{-1} for the all experiments. The exposition times used were appropriate to detect these compounds, since larger exposition saturate the detector system used. In the mechanistic study, the time used between two consecutive withdrawals was 30 minutes.

3.   Materials

The following chemicals, with purities as stated by the supplier, were used without further purification: nitrogen (Air Liquide, 99.999%), β-ocimene (Sigma-Aldrich, ≥90%), camphene (Aldrich, 95%), isobutene (Messer Griesheim, ≥99%), propene (Messer Griesheim, 99.5%) and oxalyl chloride (Sigma-Aldrich, ≥99%).

4.   Results

Rate coefficients for the reactions of Cl atoms with β-ocimene and camphene were determined by comparing their rate of decay with that of the corresponding decay of the reference compounds:

$$X + BVOC \rightarrow Products, k_{BVOC} \qquad (4)$$

$$X + Reference \rightarrow Products, k_{reference} \qquad (5)$$
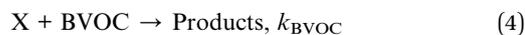
Provided that the reference compound and the reactant are lost only by reactions (4) and (5), then it can be shown that:

$$\ln\left\{\frac{[BVOC]_0}{[BVOC]_t}\right\} = \frac{k_4}{k_5}\ln\left\{\frac{[Reference]_0}{[Reference]_t}\right\} \qquad (6)$$

where $[BVOC]_0$, $[Reference]_0$, $[BVOC]_t$ and $[Reference]_t$ are the concentrations of the compounds studied and reference compound at times $t = 0$ and t, respectively, and k_4 and k_5 are the rate coefficients of reactions (4) and (5), respectively.

The relative rate technique relies on the assumption that both the monoterpenes and reference organics are removed solely by reaction with Cl atoms. To verify this assumption, various tests were performed to assess the loss of the reactants *via* reaction with oxalyl chloride, photolysis and wall deposition. These processes that could interfere with the kinetic determinations were found to be negligible for both the monoterpenes and the reference compounds. Mixtures of the monoterpenes and reference compounds with oxalyl chloride were stable in the dark when left in the chamber for the typical time span of the kinetic experiments (10–20 minutes). Moreover, in the absence of oxalyl chloride, photolysis of the mixtures (monoterpenes and reference compounds in air) did not show any decrease in the reactant concentrations over the time span of the experiments.

Fig. 1 and 2 show the kinetic data obtained from the experiments plotted according to eqn (6) for the reactions of Cl with the individual compounds studied measured relative to different reference compounds. Each plot represents a minimum of 2–3 experiments for each reference compound. Good linear relationships were obtained in all cases. The linearity of the plots with near-zero intercepts, combined with the fact that similar results were obtained for different initial concentrations of the unsaturated compound and reference organics, supports that complications due to secondary reactions in the experimental systems were negligible.

The $k_{BVOC}/k_{reference}$ ratios determined from the slopes of the straight-line plots in Fig. 1 and 2 are listed in Table 1 together with the absolute values of the rate coefficients, k_{BVOC}, calculated from the $k_{BVOC}/k_{reference}$ ratios.
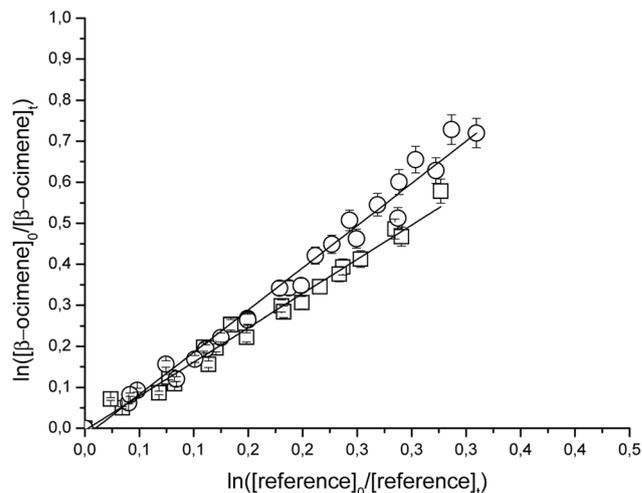

Fig. 1   Relative rate data for the reaction of Cl with β-ocimene using isobutene (□) and propene (○) as reference compounds at 298 K and atmospheric pressure of air.

In order to place on an absolute basis the rate coefficients for the reactions of Cl with the monoterpenes, the following values for the reactions of Cl with the reference compounds at 298 K were used: $(3.40 \pm 0.28) \times 10^{-10}$ cm^3 per molecule per s for Cl + isobutene[25] and $(2.64 \pm 0.21) \times 10^{-10}$ cm^3 per molecule per s for Cl + propene.[25] The errors for the ratios $k_{BVOC}/k_{reference}$ are only the 2σ statistical errors, and the errors in the k_{BVOC} was calculated using the propagation of relative error calculation method.

For both compounds, there is a good agreement between the values of k_{BVOC} determined using two different reference compounds.

Averaging the values of the rate coefficients and taking errors which encompass the extremes of both determinations for each reaction result in the following final values for the reaction rate coefficients at 298 K:
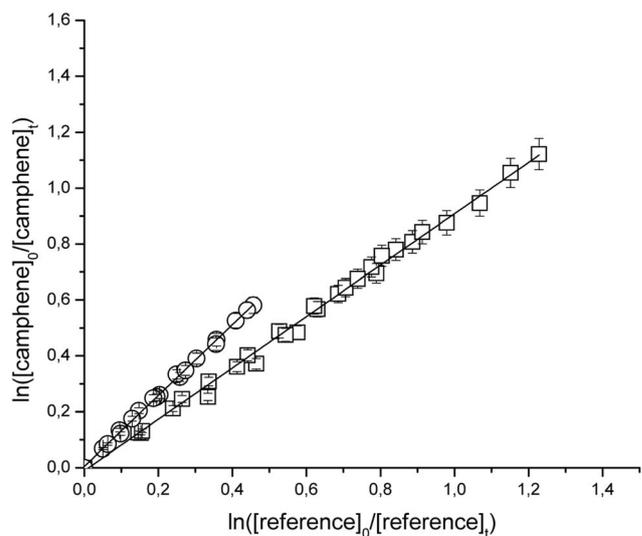

Fig. 2   Relative rate data for the reaction of Cl with camphene using isobutene (□) and propene (○) as reference compounds at 298 K and atmospheric pressure of air.

Table 1 Reference compound, measured rate coefficient ratios, $k_{BVOC}/k_{reference}$, and the obtained rate coefficients for the reactions of Cl atoms with β-ocimene and camphene at 298 K in 760 torr of air

Reaction	Reference	$k_{BVOC}/k_{reference}$	$k_{BVOC} \times 10^{10}$ (cm^3 per molecule per s)
β-Ocimene + Cl	Isobutene	1.63 ± 0.05	5.5 ± 0.6
	Isobutene	1.69 ± 0.05	5.7 ± 0.6
	Isobutene	1.63 ± 0.04	5.5 ± 0.6
	Propene	2.13 ± 0.09	5.6 ± 0.7
	Propene	1.96 ± 0.07	5.2 ± 0.6
	Propene	2.15 ± 0.07	5.7 ± 0.6
		Average	**5.5 ± 0.7**
Camphene + Cl	Isobutene	0.93 ± 0.02	3.2 ± 0.3
	Isobutene	0.93 ± 0.01	3.2 ± 0.3
	Isobutene	0.94 ± 0.02	3.2 ± 0.3
	Propene	1.26 ± 0.04	3.3 ± 0.4
	Propene	1.27 ± 0.01	3.4 ± 0.3
	Propene	1.27 ± 0.02	3.4 ± 0.3
		Average	**3.3 ± 0.4**

$$k_1 = (5.5 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ per molecule per s}$$

$$k_2 = (3.3 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ per molecule per s}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which a contribution has been added to cover uncertainties in the reference rate coefficients.

Regarding to products identification, for the reaction of β-ocimene with Cl atoms the only identified product was acetone observed as oxime due to the derivatization with PFBHA. Chromatogram and mass spectra are presented on the ESI S1a and S1b,† respectively. For the reaction of camphene with Cl atoms, the positively identified products were formaldehyde and acetone, both were observed as formaldoxime and acetoxime, the chromatogram and mass spectra are presented in the ESI S2a, b, S3a and b,† respectively.

5. Discussion

Kinetics

To the best of our knowledge, no kinetic data on the reaction of Cl atoms with β-ocimene and camphene have been reported. The present study, thus, is the first measurement of the rate coefficients of the reactions (1) and (2) and therefore no direct comparison with the literature can be made for the same reactions. However, the rate coefficients for the reaction of β-ocimene with Cl atoms ($(5.5 \pm 0.7) \times 10^{-10}$ cm^3 per molecule per s) can be compared with the rate coefficients of the reactions of myrcene + Cl atoms ($(6.6 \pm 1.5) \times 10^{-10}$ cm^3 per molecule per s),[26] taking into consideration the experimental errors, these rate coefficients present a reasonable agreement between them. On the other hand, comparing the reactivity toward Cl atoms of camphene and other bicyclic and exocyclic monoterpene, β-pinene, it can be observed that the value of the rate coefficient for the reactions of camphene + Cl atoms ($(3.3 \pm 0.4) \times 10^{-10}$ cm^3 per molecule per s) is 1.6 times lower than the rate coefficient for the reaction of β-pinene + Cl atoms ($(5.3 \pm 1.5) \times 10^{-10}$

cm^3 per molecule per s).[27] However, the structure itself of these monoterpenes has a minor influence when they react with Cl atoms, which is expected due to the reactivity of VOCs with Cl atoms is collision-controlled.

camphene   β-pinene
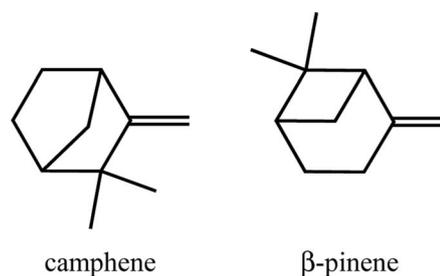
The rate coefficients of VOCs due to the reactions with Cl atoms and with OH radicals tend to present a linear correlation, in which this linearity indicates that the reaction mechanisms have similar pathway. In Fig. 3, it is shown the correlation between the rate coefficients due to reactions of OH radicals and Cl atoms with
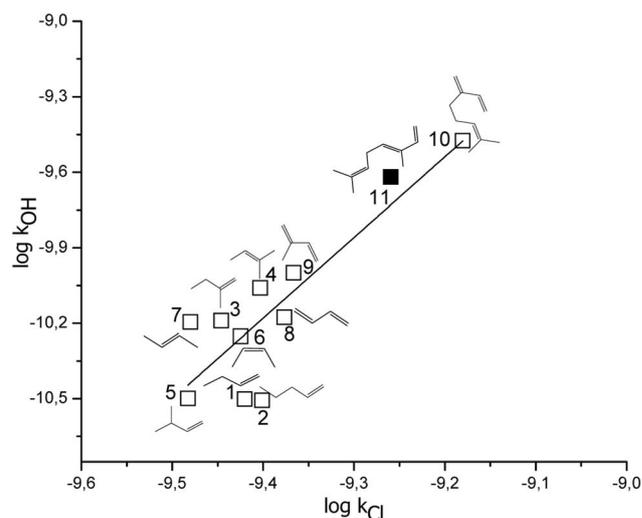

Fig. 3 Free energy correlation log k_{OH} vs. log Cl for acyclic unsaturated terpenes and alkenes, bold square correspond to β-ocimene.

Table 2 Rate coefficients for the reactions of OH radicals and Cl atoms with acyclic alkenes and terpenes at 298 K in 760 torr

No.	Compounds	$k_{OH} \times 10^{11}$ (cm³ per molecule per s)	$k_{Cl} \times 10^{10}$ (cm³ per molecule per s)
1	1-Butene	3.15[a]	3.80[d]
2	1-Pentene	3.12[a]	3.97[d]
3	2-Methyl-1-butene	6.46[a]	3.58[d]
4	2-Methyl-2-butene	8.72[a]	3.95[d]
5	3-Methyl-1-butene	3.17[a]	3.29[d]
6	(Z)-2-Butene	5.60[a]	3.76[d]
7	(E)-2-Butene	6.37[a]	3.31[d]
8	1,3-Butadiene	6.66[a]	4.20[a]
9	Isoprene	10[a]	4.30[e]
10	Myrcene	33.5[b]	6.60[f]
11	**β-Ocimene**	**24**[c]	**5.5**[c]

[a] Ref. 36. [b] Ref. 26. [c] This work. [d] Ref. 25. [e] Ref. 28. [f] Ref. 27.

acyclic alkenes and monoterpenes (these rate coefficients are presented in Table 2), where the expression obtained is the following (rate coefficient in cm³ per molecule per s, $r^2 = 0.72$):

$$\log k_{OH} = (3.2 \pm 0.6) \log k_{Cl} + (20 \pm 6)$$

A reasonable correlation has been obtained, therefore, is an indication of that the presented acyclic alkenes and monoterpenes has a similar mechanism when they react with OH radicals and Cl atoms. Additionally, in this correlation it can be observed that those compounds with a single double bond are group together, and that the reactivity increases when the compound presents two conjugated double bonds and it is even higher for the tri-unsaturated monoterpenes.

In Fig. 4, it is presented the correlation of the rate coefficients for the reactions of cyclic alkenes and terpenes with OH radicals and Cl atoms (these rate coefficients are shown in Table 3), which to our knowledge is the first correlation of this type involving cyclic compounds. The following expression has been obtained (rate coefficient in cm³ per molecule per s, $r^2 = 0.82$):

$$\log k_{OH} = (1.4 \pm 0.2) \log k_{Cl} + (3 \pm 2)$$

This correlation presents good linearity and also indicates similarity on the reaction mechanisms between the reactions of cyclic compounds with Cl atoms and OH radicals, respectively. Both correlations can be used to estimate the value of a rate coefficient when only one of them is available as experimental data.

Product identification

According to the mechanism presented in Fig. 5, the primary formation of acetone can be generated through the addition of Cl atom to the C6 and C7 in the double bond of the group $(CH_3)_2C=CH-$ in the structure of β-ocimene. However, secondary formation of acetone is also possible since β-ocimene degradation leads to the formation of several products which can also react with Cl atoms (only acetone primary formation is presented in Fig. 5).

If the addition of Cl atoms is produced in the C6 of the double bond (Fig. 5, channel A), the alcoxy radical formed could decompose forming acetone and $CH_2=CHC(CH_3)=CHCH_2CH\cdot Cl$ radical (channel A1) or decompose forming $CH_3C(CH_3)=CHCH_2CH(Cl)C(O)CH_3$ and $\cdot CH_3$ radical that could lead to the formaldehyde formation.

When the addition of Cl atoms is produced in C7 the alkoxy radical formed could generate through a decomposition $CH_2=CHC(CH_3)=CHCH_2C(O)H$ and $\cdot C(CH_3)_2Cl$ radical (channel B1) that after the subsequent reactions with O_2 in the absence of NO_x could produce $\cdot OC(CH_3)_2Cl$ radical that through an elimination of Cl atom could lead to the formation of acetone. If the alcoxy radical formed decompose by channel B2 of Fig. 5, the products formed will be $ClC(CH_3)_2C(O)H$ and $CH_2=CHC(CH_3)=CHCH_2\cdot$ radical.

According to the products identified in the experimental conditions performed in this work, we have demonstrated that the addition of Cl atoms is produced on C6–C7 of the double bond of β-ocimene leading to the formation of acetone through channels A1 and B1 of Fig. 5.

On the other hand, for the reaction of camphene with Cl atoms, the proposed reaction mechanisms is presented in
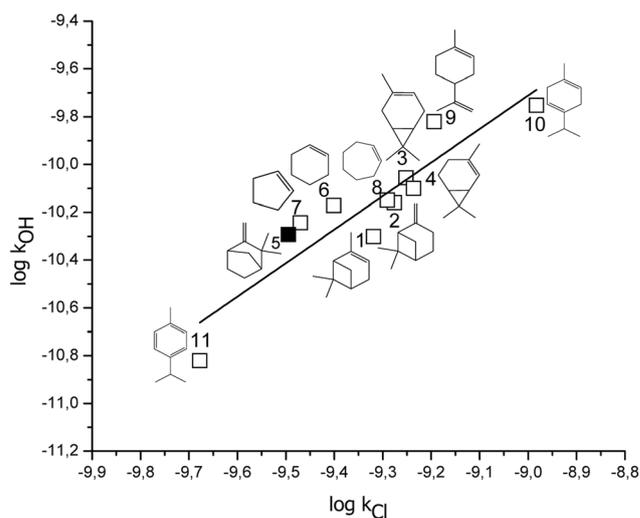

Fig. 4 Free energy correlation log k_{OH} vs. log Cl for cyclic unsaturated terpenes and alkenes, bold square correspond to camphene.

Table 3 Rate coefficients for the reactions of OH radicals and Cl atoms with cyclic terpenes and alkenes at 298 K in 760 torr

No.	Compounds	$k_{OH} \times 10^{11}$ (cm³ per molecule per s)	$k_{Cl} \times 10^{10}$ (cm³ per molecule per s)
1	α-Pinene	5.00[a]	4.80[g]
2	β-Pinene	6.92[a]	5.30[g]
3	3-Carene	8.8[b]	5.60[g]
4	2-Carene	7.95[c]	5.80[g]
5	**Camphene**	**5.1**[d]	**3.3**[d]
6	Cyclohexene	6.74[e]	3.97[b]
7	Cyclopentene	5.71[e]	3.39[b]
8	Cycloheptene	7.09[e]	5.12[b]
9	Limonene	15.9[a]	6.40[g]
10	γ-Terpinene	17.7[f]	10.4[h]
11	p-Cymene	1.51[c]	2.10[g]

[a] Ref. 37. [b] Ref. 38. [c] Ref. 39. [d] This work. [e] Ref. 36. [f] Ref. 40. [g] Ref. 27. [h] Ref. 41.

Fig. 6(a and b) by the addition of Cl atom to the C8 and C3 of this double bond, respectively. Acetone can be formed through decomposition of C2–C3 bond from the formed alkoxide when Cl atom is added to C8 (Fig. 6a), and through decomposition of C3–C8 bond from the alkoxide, which was formed due to the addition of Cl atom to C3 of the double bond (Fig. 6b), while, formaldehyde can be generated through the decomposition of C3–C8 and C3–C4 bonds from the alkoxides (Fig. 6a), and it can

also be formed due to the alkoxide decomposition C3–C8 formed from the addition of Cl atom to C3 (Fig. 6b). The degradation of these two studied monoterpenes were expected to generate acetone since they contain on their structures the $\supset C=C(CH_3)_2$ (β-ocimene) and $\supset C(CH_3)_2$ (camphene) entities, product that was also formed due to the reaction of these terpenes with OH radicals (Gaona-Colmán *et al.*, 2016a and 2017)[21,23]. Ketones and aldehydes are functional groups also
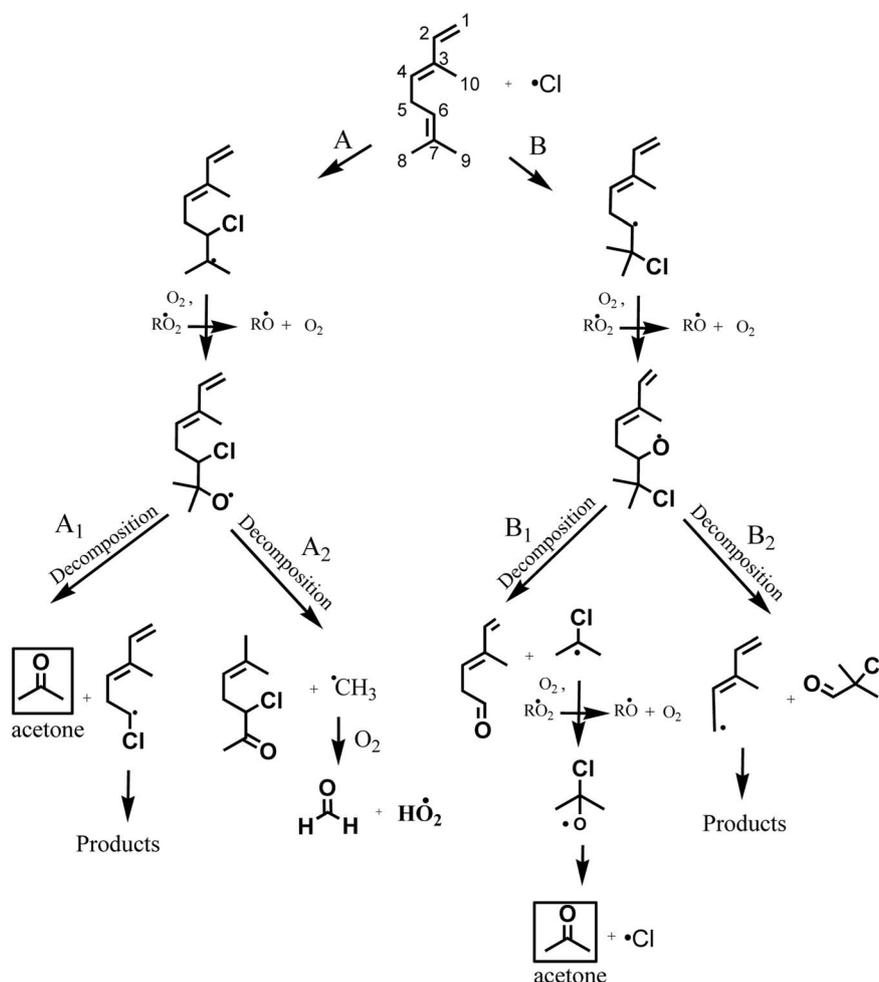

Fig. 5 Proposed reaction mechanism for β-ocimene initiated by addition of Cl atom to C6 and C7 on the double bond.
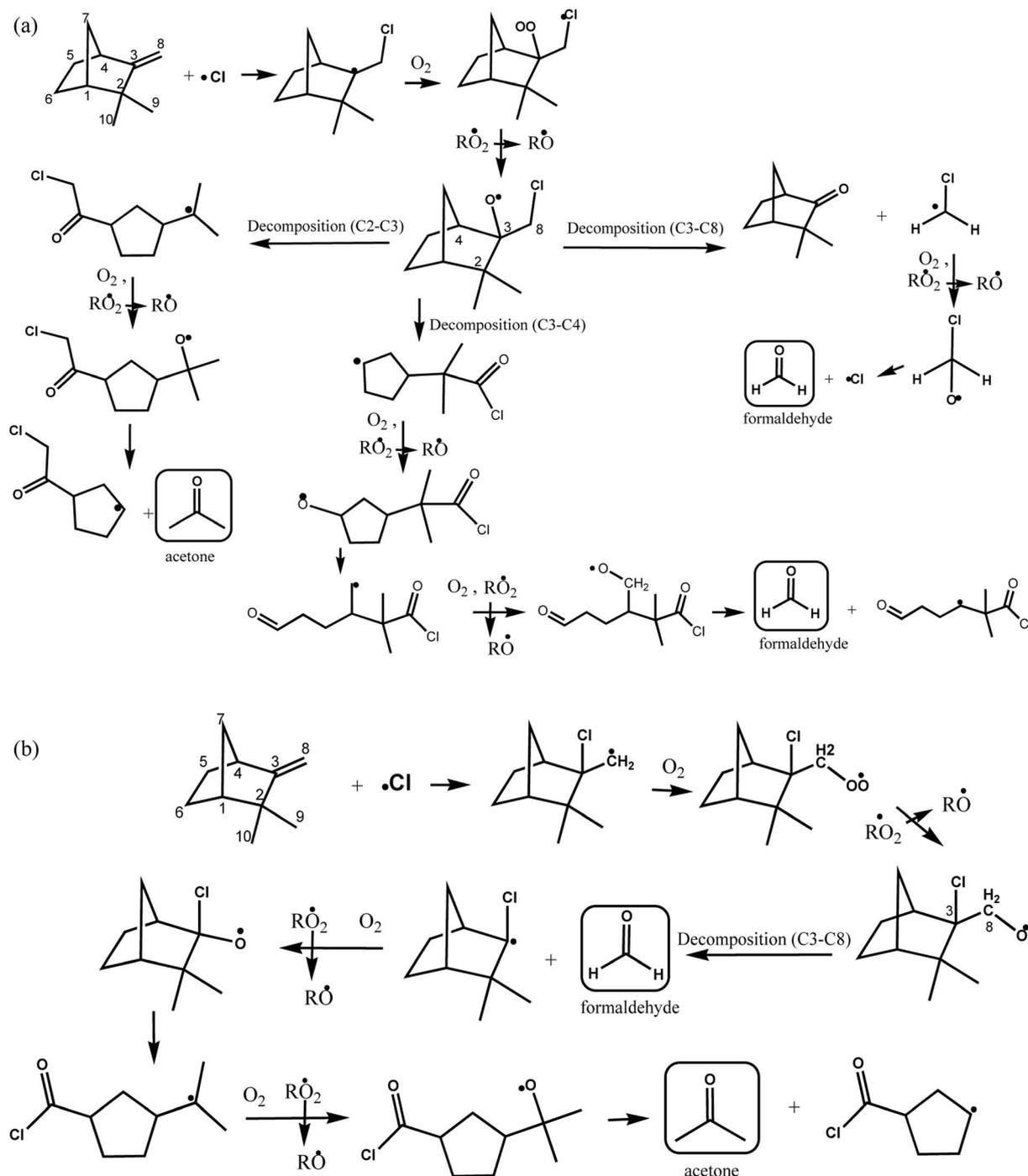
Fig. 6 (a) Proposed reaction mechanism for camphene initiated by addition of Cl atom to C8 on the double bond. (b) Proposed reaction mechanism for camphene initiated by addition of Cl atom to C3 on the double bond.

reported as products during the reaction of acyclic and cyclic alkenes with Cl atoms.[28,29]

Atmospheric implications

In Table 4 is presented the estimated tropospheric lifetimes of β-ocimene and camphene respect to their degradations toward the main atmospheric oxidants. These lifetimes have been estimated using the rate coefficients and the typical tropospheric concentrations of the oxidants: $[OH] = 2 \times 10^6$ molecules per cm^3,[30] $[O_3] = 7 \times 10^{11}$ molecules per cm^3,[31] $[NO_3] = 5 \times 10^8$ molecules per cm^3 (ref. 32) and $[Cl] = 1 \times 10^4$ molecules per cm^3.[33] Additionally, it is presented the global lifetimes taking into account the tropospheric losses of the studied compounds according to the following expression:

$$\tau_{global} = \left[\frac{1}{\tau_{OH}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{deposition}} \right]^{-1}$$

Table 4 Atmospheric lifetimes of β-ocimene and camphene with respect to its reactions with OH radicals, O_3 molecules, NO_3 radicals and Cl atoms

Compound	$k_{OH} \times 10^{11a}$	τ_{OH} (hours)	$k_{O_3} \times 10^{18a}$	τ_{O_3} (hours)	$k_{NO_3} \times 10^{13a}$	τ_{NO_3} (hours)	$k_{Cl} \times 10^{10a}$	τ_{Cl} (hours)	τ_{global} (hours)
β-Ocimene	25[b]	0.6	385[d]	1	240[g]	0.017	5.5[h]	51	0.02
	23.6[c]	0.6	556[e]	0.7					
			374[f]	1					
Camphene	5.1[i]	3	0.51[i]	778	6.54[j]	0.85	3.3[h]	84	0.7
	5.33[j]	3	0.90[j]	441					
			0.45[k]	882					

[a] k in (cm³ per molecule per s). [b] Ref. 42. [c] Ref. 21. [d] Ref. 26. [e] Ref. 43. [f] Ref. 22. [g] Ref. 44. [h] This work. [i] Ref. 23. [j] Ref. 45. [k] Ref. 46.

Since photolytic loss of β-ocimene and camphene is not relevant in the troposphere, because they do not absorb in the actinic region, and wet and dry deposition are expected to be of minor importance due to the low solubility in water and they volatility, respectively. The global tropospheric lifetimes was calculated considering the reaction with the oxidants, as it is presented in Table 4, these global lifetimes are very short for both compounds. The calculated tropospheric lifetimes due to reaction with each oxidants listed in Table 4 indicate that the reactions with OH radicals, NO_3 radicals and O_3 molecules are most important atmospheric degradation pathways for β-ocimene, while the reaction with Cl atoms could be important in regions where they are more available, i.e. coastal region or highly industrialized areas. On the other hand, the main tropospheric oxidation for camphene will occur due to reactions with OH and NO_3 radicals, and the degradation due to reactions with Cl atoms could also be important in the previously mentioned region. However, camphene loss due to reaction with O_3 is the less relevant tropospheric reactions. According to the identified products obtained in this work, the degradations of β-ocimene and camphene due to reaction with Cl atoms lead to the formation of acetone, one of the most abundant oxygenated compounds in the atmosphere. Acetone roles in the troposphere are the contribution on the HO_x cycle and the formation of peroxyacetyl nitrate, a well-known NO_x reservoir.[34] Additionally, formaldehyde was also an identified product from the reaction of camphene with Cl atoms, thus, this reaction is another photochemical source of formaldehyde in the outdoor air. This aldehyde also contributes to the HO_x cycle and is considered one of the main indoor pollutants. It is important to take into account the indoor/outdoor ratio in order to assess the risk for human health due to the exposure of formaldehyde[35] and this requires the identification all the primary and secondary sources of this aldehyde in the troposphere.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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