THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

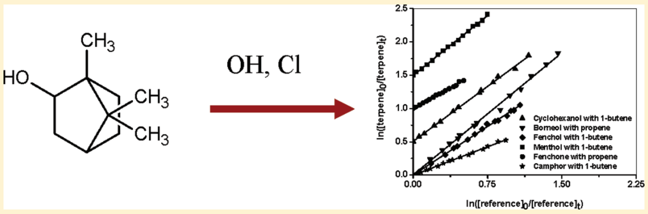
Kinetics and Mechanisms of the Tropospheric Reactions of Menthol, Borneol, Fenchol, Camphor, and Fenchone with Hydroxyl Radicals (OH) and Chlorine Atoms (Cl)

Antonio A. Ceacero-Vega,[†] Bernabé Ballesteros,[†] Iustinian Bejan,[‡] Ian Barnes,[‡] Elena Jiménez,[†]
and José Albaladejo*,[†]

[†]Departamento de Química Física, Facultad de Ciencias y Tecnología Química, Universidad de Castilla-La Mancha, Avenida Camilo José Cela, s/n. 13071 Ciudad Real, Spain

[‡]FB-C Physical Chemistry Department, University of Wuppertal, Gauss Strasse 20, 42119 Wuppertal, Germany.

ABSTRACT: Relative kinetic techniques have been used to measure the rate coefficients for the reactions of oxygenated terpenes (menthol, borneol, fenchol, camphor, and fenchone) and cyclohexanol with hydroxyl radicals (OH) and chlorine atoms (Cl) at 298 ± 2 K and atmospheric pressure. The rate coefficients obtained for the reactions of the title compounds with OH are the following (in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}): (1.48 ± 0.31), (2.65 ± 0.32), (2.49 ± 0.30), (0.38 ± 0.08), (0.39 ± 0.09) for menthol, borneol, fenchol, camphor, and fenchone, respectively. For the corresponding reactions with Cl atoms the rate coefficients are as follows (in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}): (3.21 ± 0.26), (3.40 ± 0.28), (2.72 ± 0.13), (2.93 ± 0.17), (1.59 ± 0.10), and (1.86 ± 0.29) for cyclohexanol, menthol, borneol, fenchol, camphor, and fenchone, respectively. The reported error is twice the standard deviation. Product studies of the reactions were performed using multipass in situ FTIR (Fourier transform infrared spectroscopy) and solid-phase microextraction (SPME) with analysis by GC−MS (gas chromatography−mass spectrometry). A detailed mechanism is proposed to justify the observed reaction products.



1. INTRODUCTION

Monoterpenes are a very important group of nonmethane volatile organic compounds (NMVOCs) of natural origin which are actively involved in the chemistry of the troposphere. NMVOCs of natural origin are generally referred to as biogenic volatile organic compounds (BVOCs). They are emitted in large amounts to the atmosphere in a wide variety of different forms mainly from vegetation.[1−5] BVOCs have also been detected in indoor environments due to the use of consumer cleaning products and air fresheners[6] and release from building and furnishing materials.[7] On a global scale, the emissions of BVOCs have been estimated to be 1150 TgC $year^{-1}$, of which 11% is attributed to monoterpenes.[4] In North America the total BVOC emissions have been estimated to be 84 TgC $year^{-1}$ of which 25% is allocated to monoterpenes and sesquiterpenes.[3] In Europe the estimated amounts of monoterpenes for July 2003 ranged from 338 to 1112 Gg.[8] The emissions rates of BVOCs generally depend on temperature and light intensity.[1] BVOCs are known to contribute significantly to the formation of secondary organic aerosols (SOAs)[9] and tropospheric ozone,[10,11] and thus can, depending on time and location, play an important role in the chemistry of regional-scale air pollution.[12−14] The tropospheric degradation of monoterpenes will primarily occur via reaction with OH radicals during the daytime and with NO_3 radicals at night-time. The main source of OH radicals in the atmosphere is generally assumed to be the photolysis of O_3 to generate $O(^1D)$ atoms which are either quenched to ground-state oxygen atoms, $O(^3P)$, or react with water vapor to form OH radicals,[15] although it is now recognized that the ozonolysis of alkenes and in particular the photolysis of nitrous acid (HONO) can be important sources of OH radicals, particularly in urban areas.[16]

Until fairly recently the chlorine atom initiated oxidation of NMVOCs has generally only been considered to be of importance in coastal and marine air environments and in the Arctic troposphere during springtime[17] where it is believed that the main source of chlorine atoms is the photolysis of chlorine-containing compounds generated in the heterogeneous reactions of sea-salt aerosols.[15,18,19] However, in a recent field study nitryl chloride ($ClNO_2$), a gaseous photolytic Cl atom precursor, was observed in continental regions far from coastal and marine regions, suggesting that Cl chemistry may possibly be ubiquitous in the atmosphere and play a significantly more important role than previously thought in the oxidizing capacity of the troposphere particularly in the early morning.[20]

Rate coefficients for the reactions of Cl atoms with organic compounds are generally a factor of 10 higher than the corresponding OH rate coefficients,[21,22] thus although the average concentration of chlorine atoms is much lower than that of OH radicals, the two reactions can compete with one

Received: December 14, 2011
Revised: March 21, 2012
Published: March 26, 2012

dx.doi.org/10.1021/jp212076g | J. Phys. Chem. A 2012, 116, 4097−4107

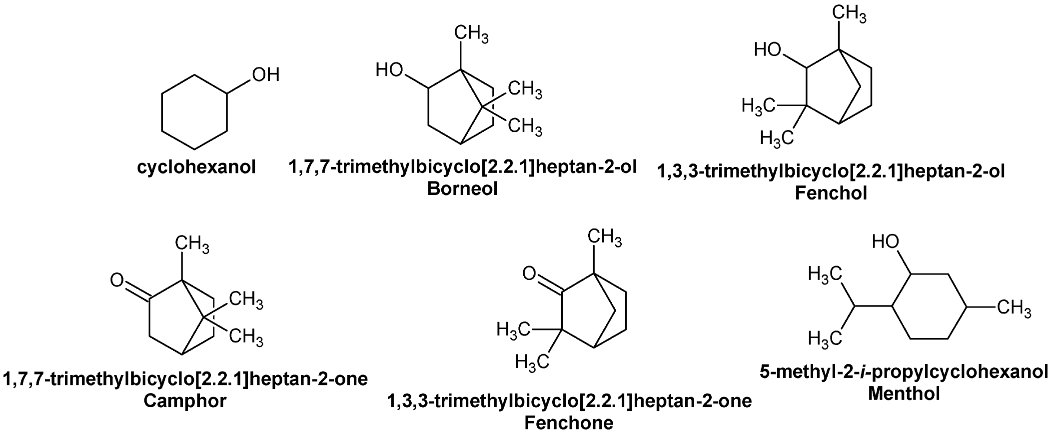


Figure 1. Structure and names, IUPAC and common, of the oxygenated terpenes and cyclohexanol studied in this work.

another in areas where the chlorine atom concentration is sufficiently high. Degradation mechanisms of VOCs initiated by OH radical and Cl atom are often very similar, in particular, for saturated VOCs. In mechanistic studies, Cl-initiated degradation is often used as a surrogate for the analogue OH reaction since the experiments with Cl atoms are generally easier to perform.

To date, kinetic and mechanistic studies on the reactions of OH, NO_3, and Cl with terpenes have mainly been focused on unsaturated species.[23−29]

In this work relative kinetic and mechanistic studies have been performed at atmospheric pressure and room temperature for the reactions of OH radicals and Cl atoms with the oxygenated terpenes: borneol, fenchol, menthol, camphor, and fenchone (Figure 1). To our knowledge, only the reactions of camphor with OH, NO_3, and O_3 have been investigated previously. Reissell et al., using relative rate methods,[30] have obtained rate coefficients (in cm^3 $molecule^{-1}$ s^{-1} units) of $(4.6 \pm 1.2) \times 10^{-12}$, $< 3 \times 10^{-16}$, and $<7 \times 10^{-20}$ for the reactions of OH, NO_3, and O_3 with camphor at 298 ± 2 K and 740 Torr total pressure of purified air, respectively. Reissell et al. also identified the products of the OH reaction. The yield for the formation of acetone was directly determined by gas chromatography to be (0.29 ± 0.04). Using *in situ* atmospheric pressure ionization tandem mass spectrometry (API-MS), they found evidence for the formation of dicarbonyl, hydroxycarbonyl, carbonyl-nitrate, and hydroxycarbonyl-nitrate compounds in the reaction system.

The structure of three of the oxygenated terpenes chosen for study in this work (borneol, fenchol, and menthol) contains the cyclohexanol structural element. The kinetics and products of the reaction of OH radicals with cyclohexanol has been investigated by Bradley et al.,[31] but to our knowledge there is no kinetic information on the reaction of Cl atoms with cyclohexanol. For this reason and for purposes of comparing the product profiles with those obtained for the oxygenated terpenes containing the cyclohexanol structure, a kinetic and product study of the reaction of chlorine atoms with cyclohexanol has also been performed.

The kinetic data obtained in this work allow establishing the dominant tropospheric removal process for the title oxygenated terpenes. In addition, the accompanying product study allows proposing a reaction mechanism for the main product forming channels.

2. EXPERIMENTAL SYSTEMS

This section has been divided into three subsections for ease of presentation. The first one briefly describes the relative rate technique used in two different laboratories at the University of Castilla-La Mancha (UCLM) and at the University of Wuppertal (UW). The experimental setups employed at UCLM and UW are described separately in subsections 2.2 and 2.3, respectively.

2.1. Relative Rate Technique.

The relative rate method is a well-established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds[23] where the decay of the compound under investigation is measured relative to the decay of a reference hydrocarbon whose rate coefficient with the oxidant is well-known. In the present study the decay of the oxygenated terpene and the reference hydrocarbon (ref) due to the reaction with the oxidant X (Cl or OH) can be described by the following reactions

$$\mathrm{OH/Cl} + \text{oxygenated terpene} \rightarrow \text{products} \quad k_i \tag{1}$$

$$\mathrm{OH/Cl} + \text{ref} \rightarrow \text{products} \quad k_{ref} \tag{2}$$

where k_i and k_{ref} are the rate coefficients for reactions of the oxidant with the oxygenated terpene and the reference hydrocarbon, respectively. Provided that the oxygenated terpene and reference hydrocarbon are lost only by reactions 1 and 2, it can be shown that

$$\ln\left(\frac{[\text{terpene}]_0}{[\text{terpene}]_t}\right) = \frac{k_i}{k_{ref}}\left(\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)\right) \tag{3}$$

where $[\text{terpene}]_0$, $[\text{reference}]_0$, $[\text{terpene}]_t$, and $[\text{reference}]_t$ are the concentrations of the oxygenated terpene and the reference hydrocarbon at times $t = 0$ and t, respectively. According to eq 3, the linear least-squares analysis of $\ln([\text{terpene}]_0/[\text{terpene}]_t)$ against $\ln([\text{reference}]_0/[\text{reference}]_t)$ plots yields k_i/k_{ref} from the slope and a zero intercept. Provided that k_{ref} is known, the rate coefficient of the reactions 1, k_i, can then be determined by multiplying the slope by k_{ref}.

Equation 3 relies on the assumption that both the oxygenated terpene and the reference hydrocarbon are removed solely by reaction with the oxidant (Cl or OH). To verify this assumption, various tests were performed to assess possible complications in the experiments through reaction of the reactants with the radical precursors (Cl_2, $SOCl_2$, H_2O_2, or CH_3ONO), photolysis, and reactant loss on the walls. These tests are previously described by Ceacero-Vega et al. for the reactions of the oxidants with 1,8-cineole,[32] and they showed that the potential interferences for both the oxygenated terpenes and the reference hydrocarbons are negligible.

In a chemical reaction the yield of a primary product B, α, is given by the ratio between the formation rate of B and the disappearance rate of the terpene:

$$\alpha = \frac{\frac{d[B]}{dt}}{-\frac{d[\text{terpene}]}{dt}} \tag{4}$$

However, B can subsequently react with the oxidants (OH/Cl); therefore, in order to obtain the correct concentration of B formed in the reaction, the measured concentration has been corrected by the amount of B consumed by the oxidant. This method is described in detail in various publications.[33−35] The concentration correction factor F is given by the following expression

$$F = \frac{k_i/k_p}{k_i} \times \frac{1 - \frac{[\text{terpene}]_t}{[\text{terpene}]_0}}{\left(\frac{[\text{terpene}]_t}{[\text{terpene}]_0}\right)^{k_p/k_i} - \frac{[\text{terpene}]_t}{[\text{terpene}]_0}} \tag{5}$$

where k_i is the rate coefficient for the reaction of oxygenated terpene with the oxidant (OH or Cl), and k_p is the rate coefficient for the reaction of the primary product with the oxidant. The slopes of plots of the corrected product concentration versus the amount of reacted oxygenated terpene will give the product yield.

2.2. Experimental Systems at the University of Castilla-La Mancha (UCLM). The experimental systems at UCLM consist of two environmental chambers equipped with FTIR or GC-MS and GC-FID analytical techniques. A detailed description of the chamber setup with FTIR has previously been presented for studies on the reaction of Cl atoms with linear and branched alcohols, and that of the chamber setup with GC-MS and GC-FID for the reaction of Cl atoms with THP (tetrahydropyran);[36,37] therefore, only a brief description of the chamber experimental systems is given here. The reaction chamber with FTIR as the detection method consists of a 16 L borosilicate glass cylinder containing a multipass optical reflection system, which is coupled to a Nexus Thermo Nicolet FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector for online infrared spectroscopy. A total path length of 96 m was used, and infrared spectra were obtained by coadding 64 scans with a resolution of 2 cm^{-1}. The chamber is surrounded by 4 evenly spaced UV fluorescent lamps (Philips TL-K 40 W, λ_{max} = 365 nm) that continuously irradiate the gas sample. Liquid and gaseous compounds were introduced directly into the cell by expansion from a glass manifold system and mixed in synthetic air or helium at 298 ± 2 K and 720 ± 5 Torr of total pressure. Compounds in the solid state or liquids with a low vapor pressure were introduced into the chamber by flowing the bath gas through a heated glass bulb which contained the compounds.

The experimental system with GC-MS and GC-FID analytical methods consisted of either a 100 or 200 L Teflon bag, surrounded by 8 lamps emitting in the visible (Philips TL 40 W, λ_{max} = 365 nm) and 8 UV lamps (Philips TUV G 36 W, λ_{max} = 254 nm).[36] Gas samples from the reactor were analyzed by a GC (Thermo Electron Co., model Trace GC Ultra) coupled to a mass spectrometer (Thermo Electron Co., model DSQ II) or a FID (flame ionization detector). Chlorine atoms were produced by either the photolysis of Cl_2 or $SOCl_2$ in the bath gas (synthetic air or He), and OH radicals by the photolysis of H_2O_2. Experiments were also performed in the absence of radiation to check for dark reactions and wall losses.

Products studies on the reactions of OH and Cl with cyclohexanol, borneol, and fenchol were performed in the 200 L Teflon bag at 298 ± 2 K and 720 ± 5 Torr total pressure of synthetic air, using the solid-phase microextraction sampling technique (SPME) and analysis with GC−MS and FID. SPME is a sampling technique which does not use a solvent and has been shown to be very effective in the study of organic compounds.[32,38−44] In this work, a 50/30 μm divinylbenzene/carboxen/polydimethylsyloxane fiber is used, which was exposed during experiments to the chamber contents for typically 20 min. The absorbed compounds were then desorbed at 270 °C in the heated injection port of the GC-MS instrument. Identification of reaction products was made by comparison of the mass spectra with a library of mass spectra and the mass spectra of commercial samples when available. For quantification of the product yields, SPME sampling in conjunction with the GC-FID system was used. Tests were made to ensure that the FID response was linear to the detected reactant/product over the range of concentrations used in the experiments.

2.3. Experimental Systems at the University of Wuppertal (UW). Only a brief description of the experimental systems at UW is given here since the systems have been described in detail elsewhere.[45−47] The experiments were performed at 298 ± 2 K and 760 ± 10 Torr total pressure of synthetic air or nitrogen in two cylindrical reactors, a 1080 L quartz glass and a 480 L borosilicate glass chamber, each closed at both ends by aluminum flanges. Each chamber is equipped with a pumping system consisting of a turbo-molecular pump backed by a double-stage rotary fore pump which enables the reactors to be evacuated to about 10^{-3} Torr. Magnetically coupled Teflon mixing fans are mounted inside each chamber to ensure homogeneous mixing of the reactants with the bath gas. The photolysis system for the 1080 L reactor consists of 32 superactinic fluorescent lamps (Philips TL05 40 W: 320−480 nm, λ_{max} = 360 nm), which are spaced evenly around the reaction vessel while for the 480 L reactor it consists of 20 such lamps which are likewise spaced evenly around the chamber.

The chambers each contain a White type multiple-reflection mirror system for sensitive in situ long path absorption monitoring of reactants and products in the IR spectral range 4000−700 cm^{-1}. The White systems are set for total optical path lengths of 51.6 and 484.7 m in the 480 and 1080 L chamber, respectively. IR spectra were recorded with a spectral resolution of 1 cm^{-1} using Nicolet Magna 550 (480 L reactor) and Nicolet Nexus (1080 L reactor) FTIR spectrometers each equipped with liquid nitrogen cooled MCT detectors.

Chlorine atoms were generated by the photolysis of Cl_2, and OH radicals were generated by the photolysis of CH_3ONO in the presence of NO. As described in subsection 2.1, experiments were performed to test for complicating factors such as reaction with radical precursors, photolysis, or wall loss of the compounds under investigation. The tests showed that such potential interferences were negligible.

2.3. Chemicals and Reactant Concentrations. The chemical purities of the reagents used were as follows: synthetic air (Praxair, 99.999%), 1-butene (Messer Griesheim, grade 2.0), propene (Messer Griesheim, 2.8; Praxair 99.8%), 1,3-butadiene

(Aldrich, 99%), camphor (Sigma-Aldrich, ≥ 95%), borneol (Sigma-Aldrich, ≥ 99%), Cl_2 (Messer Griesheim, 99.8%, Praxair 99.999%), fenchol (Sigma-Aldrich, > 97), fechone (Sigma-Aldrich, ≥ 99.5%), H_2O_2 (Scharlau, 50%), He (Praxair, 99.995%), nitrogen (Air Liquide, 99.999%), synthetic air (Air Liquide, 99.99%, and Praxair 99.99%), NO (Praxair, 99.999%), *n*-octane (Sigma-Aldrich, ≥ 99.0%), $SOCl_2$ (Sigma-Aldrich, ≥ 99.0%), tetrahydropyran (Sigma-Aldrich, 99%), cyclohexane (Sigma-Aldrich, 99%), cyclohexanol (Sigma-Aldrich, 99%). All compounds were used without further purification.

The initial concentration ranges used in the experiments performed at UCLM and UW were (0.6−11.7) ppmV for the oxygenated terpenes, (1.1−46.4) ppmV for the reference compounds, (1.8−24.7) ppmV for Cl_2, (4.4−11.7) ppmV for $SOCl_2$, (23.2−46.4) ppmV for H_2O_2, and (1.9−22.3) ppmV for NO.

3. RESULTS AND DISCUSSION

3.1. Relative Rate Coefficients for OH Reactions. The experimental data obtained from the kinetic investigations on the reactions of OH with borneol and fenchol at UW and menthol, camphor, and fenchone at UCLM have been analyzed in accordance with eq 3. Figure 2 (lower plot) shows several examples of plots of eq 3 for these OH-reactions where propene or 1-butene was used as reference compound. For all compounds the plots show good linearity and pass through the origin.

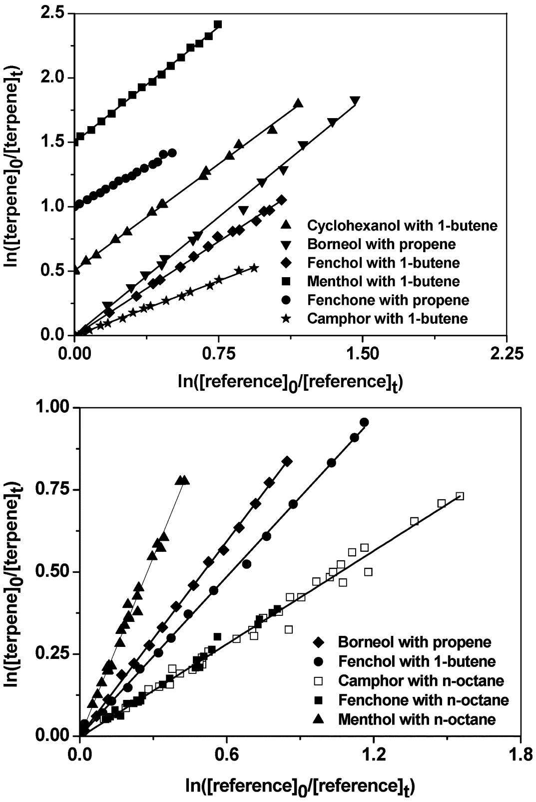


Figure 2. Examples of relative rate data for the reactions of OH (lower) and Cl atoms (upper) with oxygenated terpenes using different reference compounds. For clarity the near-zero *y*-intercepts have been shifted on some plots.

The slope of such plots corresponds to the rate coefficient ratio k_i/k_{ref}. The values of k_i/k_{ref} extracted from linear-least-squares analyses of these plots are summarized in Table 1.

The absolute rate coefficients for the OH-reaction with the oxygenated terpenes given in Table 1 have been obtained by multiplying the rate coefficient ratio with the appropriate value of the rate coefficient for reaction of OH with the reference compound. Rate coefficients used ($\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) at 298 K for the OH-reaction with 1-butene, propene, and *n*-octane were (3.14 ± 0.62), (2.63 ± 0.39),[48] and 8.11,[23] respectively. Table 1 shows rate coefficients obtained with two different reference hydrocarbons that are in excellent agreement; therefore, the reported rate coefficient for these reactions is the average of the individual determinations. Thus, k_i for the reactions of the oxygenated terpenes with OH at 298 K and 720 Torr total pressure are the following (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}): (2.65 ± 0.32) for borneol, (2.49 ± 0.30) for fenchol, (1.48 ± 0.31) for menthol, (0.38 ± 0.08) for camphor, and (0.39 ± 0.08) for fenchone, as Table 1 shows.

The rate coefficients obtained for the bicyclic oxygenated terpenes studied in this work are of the same order of magnitude as those for bicylic alkanes of similar size such as bicyclo[2.2.2]octane, bicyclo[3.3.0]octane, bicyclo[2.2.1]heptane, *cis*-bicyclo[4.3.0]nonane, and *trans*-bicyclo[4.3.0]nonane where values in the range (0.51−1.65) × 10^{-11} cm^3 molecule^{-1} s^{-1} have been reported.[23] The rate coefficient for the reaction of OH with 1,8-cineole at 293 K and 760 Torr total pressure reported by our research groups[32] is also of the same order of magnitude, (1.04 ± 0.12) × 10^{-11} cm^3 molecule^{-1} s^{-1}.

Rate coefficients for the reactions of OH with the oxygenated terpenes can only be compared with the previous study on the reaction of OH with camphor by Reissell et al.[30] They reported a rate coefficient of (0.46 ± 0.12) × 10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of OH with camphor, which is in agreement with the value obtained in this work. The rate coefficient obtained for the reaction of OH radicals with fenchone is very similar to that for camphor, which is expected since they both have very similar structures.

For the remaining of the oxygenated terpenes, k_i can be compared with that of the reaction of OH with cyclohexanol, which has a similar but simpler structure than borneol, fenchol, and menthol. As mentioned in the Introduction, Bradley et al. reported a rate coefficient of (1.90 ± 0.05) × 10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of OH with cyclohexanol at 293 K and 760 Torr total pressure.[31] This value is similar to the values obtained in the present work for the alcoholic terpenes (menthol, borneol, and fenchol).

A rate coefficient of (6.97 ± 1.39) × 10^{-12} cm^3 molecule^{-1} s^{-1} is reported in the literature for the reaction of OH with cyclohexane.[23] This value is only slightly higher than the value of (6.39 ± 0.12) × 10^{-12} cm^3 molecule^{-1} s^{-1} reported for the reaction of OH with cyclohexanone by Dagaut et al.,[49] whereas for cyclohexanol and menthol the rate coefficients are significantly higher, (1.90 ± 0.05) × 10^{-11} cm^3 molecule^{-1} s^{-1}[31] and (1.58 ± 0.32) × 10^{-11} cm^3 molecule^{-1} s^{-1} (this work), respectively. Whereas the ketone group has a deactivating −I effect on the OH reactivity, Nelson et al. reported that the −OH group in linear alcohols has a long-range activating effect on reactivity that can stretch over five carbon atoms.[50] The same tendency would seem to apply for the bicyclic oxygenated terpenes (borneol, fenchol, camphor, and fenchone). The rate coefficients for these compounds are also much higher than that of 5.12 × 10^{-12} cm^3 molecule^{-1} s^{-1}

Table 1. Rate Coefficients for the Reactions of Oxygenated Terpenes with OH Radicals at 298 K and 720 Torr of Pressure in Air[a]

terpene	exptl syst	ref	detection technique	OH source	$(k_i/k_{ref}) \pm 2\sigma$	$(k_i \pm 2\sigma) \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1})	$(k_i \pm 2\sigma) \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1}) average
borneol	UW[b] (480 L)	1-butene	FTIR	CH_3ONO/NO	0.84 ± 0.01	2.64 ± 0.53	2.65 ± 0.32
	UW[b] (480 L)	propene	FTIR	CH_3ONO/NO	1.01 ± 0.01	2.66 ± 0.38	
fenchol	UW[b] (480 L)	1-butene	FTIR	CH_3ONO/NO	0.81 ± 0.01	2.54 ± 0.51	2.49 ± 0.30
	UW[b] (480 L)	propene	FTIR	CH_3ONO/NO	1.01 ± 0.01	2.47 ± 0.37	
menthol	UCLM[c] (200 L)	n-octane	GC-FID/SPME	H_2O_2	1.83 ± 0.08	1.48 ± 0.31	1.48 ± 0.31
camphor	UCLM[c] (200 L)	n-octane	GC-FID/SPME	H_2O_2	0.47 ± 0.02	0.38 ± 0.08	0.38 ± 0.08
fenchone	UCLM[c] (200 L)	n-octane	GC-FID/SPME	H_2O_2	0.48 ± 0.02	0.39 ± 0.09	0.39 ± 0.09

[a] $k_{1\text{-butene}} = (3.14 \pm 0.62) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; $k_{propene} = (2.63 \pm 0.39) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[48] $k_{n\text{-octane}} = 8.11 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[23] [b] UW: University of Wuppertal. [c] UCLM: University of Castilla − La Mancha.

Table 2. Rate Coefficients for the Reactions of Cyclohexanol, Menthol, Borneol, and Fenchol with Cl atoms at 298 K and 720 Torr, using FTIR as Detection Technique and Cl_2 as Cl Source[a]

compd	exptl syst	ref	bath gas	$(k_i/k_{ref}) \pm 2\sigma$	$(k_i \pm 2\sigma) \times 10^{10}$ (cm^3 $molecule^{-1}$ s^{-1})	$(k_i \pm 2\sigma) \times 10^{10}$ (cm^3 $molecule^{-1}$ s^{-1}) average
cyclohexanol	UCLM[b] (16 L)	propene	air	1.44 ± 0.01	3.21 ± 0.45	3.21 ± 0.26
	UCLM[b] (16 L)	propene	He	1.44 ± 0.02	3.21 ± 0.45	
	UCLM[b] (16 L)	1-butene	air	1.09 ± 0.01	3.20 ± 0.46	
menthol	UW[c] (480 L)	1-butene	air	1.17 ± 0.01	3.44 ± 0.49	3.40 ± 0.28
	UCLM[b] (16 L)	propene	air	1.51 ± 0.02	3.36 ± 0.47	
	UCLM[b] (16 L)	propene	He	1.53 ± 0.04	3.40 ± 0.48	
borneol	UW[c] (480 L)	1-butene	air	0.89 ± 0.01	2.62 ± 0.38	2.72 ± 0.13
	UW[c] (480 L)	1-butene	N_2	0.91 ± 0.01	2.67 ± 0.38	
	UW[c] (480 L)	propene	air	1.23 ± 0.01	2.74 ± 0.38	
	UCLM[b] (16 L)	propene	air	1.22 ± 0.02	2.72 ± 0.38	
	UCLM[b] (16 L)	propene	He	1.25 ± 0.02	2.79 ± 0.38	
	UCLM[b] (16 L)	1-butene	air	0.92 ± 0.02	2.70 ± 0.39	
	UCLM[b] (16 L)	1,3-butadiene	air	0.66 ± 0.01	2.76 ± 0.27	
	UCLM[b] (16 L)	cyclohexane	air	0.89 ± 0.02	2.73 ± 0.55	
fenchol	UW[c] (1080 L)	1-butene	air	0.98 ± 0.01	2.88 ± 0.41	2.93 ± 0.17
	UW[c] (1080 L)	1-butene	N_2	0.98 ± 0.02	2.88 ± 0.42	
	UW[c] (1080 L)	propene	air	1.28 ± 0.02	2.86 ± 0.40	
	UCLM[b] (16 L)	propene	air	1.29 ± 0.02	2.96 ± 0.30	
	UCLM[b] (16 L)	1-butene	air	1.03 ± 0.02	3.03 ± 0.44	

[a] $k_{propene} = (2.23 \pm 0.31) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}; $k_{1\text{-butene}} = (2.94 \pm 0.42) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.[21] $k_{1,3\text{-butadiene}} = (4.20 \pm 0.40) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.[54] $k_{cyclohexane} = (3.08 \pm 0.12) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.[55] [b] UCLM: University of Castilla − La Mancha. [c] UW: University of Wuppertal.

reported for the reaction of OH with the alkane bicyclo[2.2.1]-heptane[23] which has a similar carbon number. The reaction of OH radicals with the oxygenated terpenes proceeds by hydrogen atom abstraction from the various $-CH_n-$ groups ($n = 1-3$) in the compounds. The magnitude of the OH rate coefficients for the oxygenated terpenes will depend on the number of primary, secondary, and tertiary H-atoms in the carbon skeleton and the effect neighboring substituent has on their OH reactivity. This is the premise of the structure and activity relationship (SAR) method[51] for estimating rate coefficients.

The SAR estimated rate coefficients for menthol, borneol, fenchol, camphor, and fenchone are the following (in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}): 2.79, 1.64, 1.40, 0.99, and 1.19, respectively. In the SAR calculations for menthol, borneol, and fenchol, the updated substituent factors for effects of OH substituent on H-atom abstraction at the α- and β-positions as reported by Bethel et al.[52] have been used. The measured rate coefficient for OH with the monocyclic alcohol menthol is overestimated by the SAR whereas for the bicyclic alcohols borneol and fenchol it is underestimated. For the bicyclic ketones, camphor and fenchone, the measured rate coefficients are factors of ~2.5 lower than the calculated SAR values.

The SAR of Kwok and Atkinson[51] includes a factor to account for activation of H-atom abstraction from C−H bonds on the β-carbon to the carbonyl group, which is attributed to the formation of a hydrogen-bonded transition state. However, a recent study on the reaction of OH with cycloketones[53] concluded that this β-activation is absent in cyclopentanone and cyclohexanone but occurs for cyclooctanone and cycloheptanone. This conclusion is in agreement with the discussion of Dagaut et al.[49] The cyclic ketones investigated in this study, camphor and fenchone, have each two C5 rings. If the rate coefficients for OH with camphor and fenchone are calculated with the Kwok and Atkinson SAR without incorporation of a β-activation factor, a rate coefficient of 0.58×10^{-11} cm^3 $molecule^{-1}$ s^{-1} is obtained for both reactions which is in excellent agreement with the measured rate coefficients and vindicates the conclusions on β-activation in ring systems reported by Dagaut et al.[49] and Aschmann et al.[53]

Table 3. Rate Coefficients Obtained for the Reactions of Camphor and Fenchone with Chlorine Atoms at 298 K and 720 Torr of Pressure[a]

compd	exptl syst	ref	bath gas	detection technique	Cl source	$(k_i/k_{ref}) \pm 2\sigma$	$(k_i \pm 2\sigma) \times 10^{10}$ (cm^3 molecule^{-1} s^{-1})	$(k_i \pm 2\sigma) \times 10^{10}$ (cm^3 molecule^{-1} s^{-1}) average
camphor	UW[b] (1080 L)	propene	air	FTIR	Cl_2	0.70 ± 0.01	1.56 ± 0.22	1.59 ± 0.10
	UW[b] (1080 L)	propene	N_2	FTIR	Cl_2	0.70 ± 0.01	1.56 ± 0.22	
	UW[b] (1080 L)	1-butene	air	FTIR	Cl_2	0.57 ± 0.01	1.68 ± 0.24	
	UCLM[c] (16 L)	propene	air	FTIR	Cl_2	0.70 ± 0.01	1.56 ± 0.22	
	UCLM[c] (16 L)	1-butene	air	FTIR	Cl_2	0.55 ± 0.01	1.62 ± 0.23	
fenchone	UW[b] (1080 L)	1-butene	air	FTIR	Cl_2	0.63 ± 0.01	1.85 ± 0.27	1.86 ± 0.29
	UW[b] (1080 L)	propene	N_2	FTIR	Cl_2	0.64 ± 0.01	1.88 ± 0.27	
	UW[b] (480 L)	1-butene	air	FTIR	Cl_2	0.61 ± 0.01	1.80 ± 0.26	
	UCLM[c] (16 L)	propene	air	FTIR	Cl_2	0.82 ± 0.02	1.83 ± 0.26	
	UCLM[c] (200 L)	tetrahydropyran	air	SPME/GC-MS	$SOCl_2$	0.78 ± 0.03	1.72 ± 0.26	
	UCLM[c] (200 L)	tetrahydropyran	He	SPME/GC-MS	$SOCl_2$	0.84 ± 0.06	1.86 ± 0.30	

[a] $k_{propene} = (2.23 \pm 0.31) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $k_{1\text{-butene}} = (2.94 \pm 0.42) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[21] $k_{tetrahydropyran} = (2.21 \pm 0.32) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[36]. [b] UW: University of Wuppertal. [c] UCLM: University of Castilla − La Mancha.

All the compounds have the same number of $-CH_3$ and $-CH_2-$ groups, but they differ in the number of available $>CH-$ groups: one for camphor and fenchone, two for borneol and fenchol, and four for menthol. On this basis, one would expect menthol to be the most reactive compound, borneol and fenchol to be similar in reactivity and slightly slower, and camphor and fenchone to be the slowest and also similar in reactivity. Except for menthol, the observed reactivity follows this trend. The reason for the higher reactivity of the bicyclic compounds, borneol and fenchol, toward OH compared to menthol is not presently clear. Further measurements are necessary to validate the rate coefficients reported here for the reactions of OH with these compounds before any definitive conclusions regarding the reactivity trend can be made.

3.2. Relative Rate Coefficients for Cl Reactions. Figure 2 (upper) shows examples of the kinetic data obtained from investigations on the reactions of the oxygenated terpenes with Cl atoms plotted according to eq 3. The plots for all of the compounds show good linearity and pass through the origin. k_i/k_{ref} rate coefficient ratios obtained for cyclohexanol and the oxygenated terpenes from the linear least-squares analysis of the kinetic data are listed in Tables 2 and 3. The rate coefficients for the reactions of the title compounds with Cl were put on an absolute basis using the following values (in units 10^{-10} cm^3 molecule^{-1} s^{-1}) for the reactions of Cl with the reference compounds: propene (2.23 ± 0.31),[21] 1-butene (2.94 ± 0.42),[21] 1,3-butadiene (4.20 ± 0.40),[54] and cyclohexane (3.08 ± 0.12).[55] Tables 2 and 3 show the rate coefficients obtained from experiments performed in different reactors and bath gases, and using different reference compounds. k_i was observed to be independent of those experimentally, and therefore, an average of the individual determinations is also reported in Tables 2 and 3.

The rate coefficient of $(3.21 \pm 0.26) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} obtained for the reaction of Cl with cyclohexanol can be compared with the rate coefficients for the reactions of Cl atoms with the linear alcohols hexanol and 1-heptanol which have a similar number of carbon atoms. Nelson et al. have reported rate coefficients of (2.90 ± 0.09) and $(3.49 \pm 0.18) \times 10^{-10}$ cm^3 molecule^{-1}s^{-1} for the reactions of Cl with 1-hexanol and 1-heptanol, respectively.[50] The rate coefficient obtained in this work for cyclohexanol with chlorine atoms is in good agreement with these values.

As for reactions of the oxygenated terpenes with OH, the reactivity of these compounds toward Cl atoms will be mainly determined by the types of abstractable H-atoms. On this basis, one would expect the following reactivity trend: menthol > borneol ≈ fenchol > camphor ≈ fenchone. As can be seen in Tables 2 and 3, that is the experimentally observed trend.

The rate coefficients for the reactions of Cl with camphor and fenchone can be compared with the rate coefficient for the reaction of Cl with cyclohexanone. An averaged published value of $(1.74 \pm 0.15) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}[56−58] is available for this reaction which is similar to the rate coefficient measured in this work for the reaction of fenchone and camphor with Cl atoms. The rate coefficients for all the oxygenated terpenes are of the same order of magnitude as that measured for the reaction of chlorine atoms with 1,8-cineole of $(2.20 \pm 0.11) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[32]

Using the SAR method developed for estimating rate coefficients for the reactions of Cl with organics,[55] the estimated rate coefficient for cyclohexanol (2.94×10^{-10} cm^3 molecule^{-1} s^{-1}) is in very good agreement with the experimentally determined one. A substituent factor for the OH alcoholic group of 0.90, which has been derived from several reactions of aliphatic alcohols with Cl, was used in that estimation. Similar agreement is found for the reactions of Cl with menthol, borneol, and fenchol where the SAR estimated k (in 10^{-10} cm^3 molecule^{-1} s^{-1} units) values are 3.29, 2.99, and 2.99, respectively. However, for camphor and fenchone the SAR method provides values of 2.24×10^{-10} cm^3 molecule^{-1} s^{-1}, and 2.65×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively, when using a factor of 0.17 for the contribution of the carbonyl group to the reactivity derived from the rate coefficient of cyclohexanone with chlorine atoms,[56−58] which are somewhat higher than the corresponding values obtained experimentally in this work.

4. PRODUCT STUDIES AND MECHANISM

Product studies have been performed on the reactions of Cl atoms and OH radicals with borneol and fenchol by irradiation of oxygenated terpene/Cl_2/air or oxygenated terpene/H_2O_2/air mixtures at 298 K and 720 Torr total pressure. A product study has also been performed for the reaction of chlorine atoms with cyclohexanol. Reaction products, once identified, were corrected for secondary consumption using eq 5, and their yields were then extracted from plots of the corrected concentration of the products versus the amount of reacted oxygenated terpene (or cyclohexanol). With all the experimental results and well-established VOC degradation pathways in the atmosphere,[15] mechanisms have been elucidated for the reactions of OH radicals and Cl atoms with borneol (see below).

4.1. Product Study on the Cl + Cyclohexanol Reaction.

Figure 3 shows an example of a gas chromatogram of a sample taken before and after irradiation of a cyclohexanol/Cl_2/air mixture in the 200 L chamber at UCLM. Cyclohexanone, chlorocyclohexane, and cyclohexene were identified by comparison of their mass spectrum with the corresponding spectra from a spectral library and also the mass spectrum generated experimentally from a commercial sample of the compound. Cyclohexanone is present as an impurity in cyclohexanol. This initial amount of cyclohexanone was considered in the yield corrections.

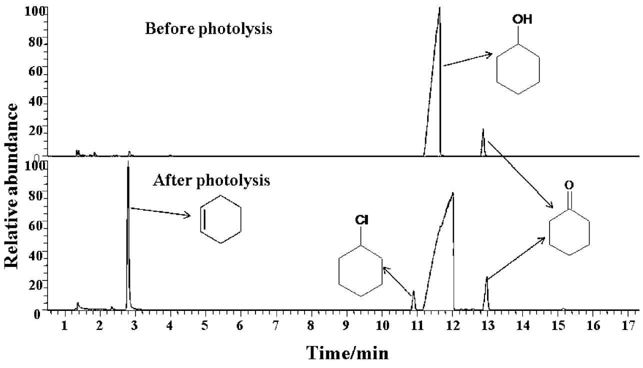


Figure 3. Gas chromatograms of samples from a Cl_2/cyclohexanol/air reaction mixture before and after photolysis.

Figure 4 shows plots of the corrected and uncorrected concentrations of cyclohexanone versus the amount of reacted cyclohexanol. The secondary consumption of cyclohexanone was corrected according to eq 5, assuming a rate coefficient k_p for cyclohexanone to be $(1.75 \pm 0.15) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.[56−58] The maximum correction factor F was 1.43. The yield of cyclohexanone in the Cl-reaction is (9.1 ± 0.6)%, where the reported error is twice the standard deviation. Bradley et al. reported a cyclohexanone yield of (55.0 ± 0.6)% for the reaction of OH radicals with cyclohexanol[31] which is much higher than the value for reaction with chlorine atoms measured in this work. This difference is probably due to the fact that reactions of Cl atoms with VOCs are much less site specific than the corresponding OH radical reactions. The SAR method estimates that approximately 11% and 58% of the Cl and OH reactions, respectively, will occur at the H from tertiary carbon site which is in accordance with the reported cyclohexanone yield in this work and that of Bradley et al.

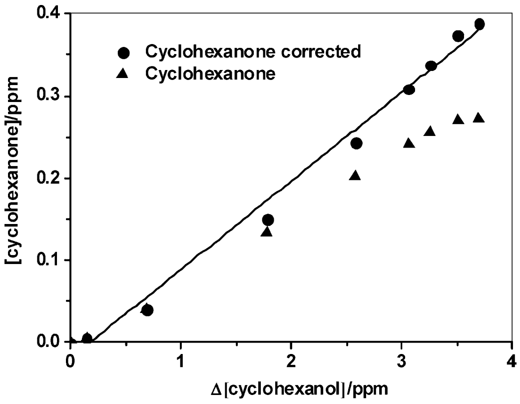


Figure 4. Plot of the concentration of cyclohexanone formed in the reaction of Cl atoms with cyclohexanol as a function of the amount of reacted cyclohexanol with and without correction for secondary reactions using eq 5.

Cyclohexanone is detected as main product of reaction. The formation of cyclohexanone is initiated by the abstraction of a tertiary hydrogen atom from the >CHOH− entity of cyclohexanol to give the 1-hydroxycyclohexyl radical which reacts immediately with O_2 to give cyclohexanone and a HO_2 radical. A similar mechanism has been proposed for the formation of cyclohexanone from the reaction of cyclohexanol with OH radicals.[31] Cyclohexene and chlorocyclohexane are detected as minor product of the reaction. The source of these compounds is currently unknown, but it is suspected that they are formed heterogeneously.

4.2. Product Study of the Reactions of Borneol and Fenchol with OH Radicals.

Product studies were performed on the reactions of borneol and fenchol with OH radicals in the 200 L reactor at UCLM at 298 K and 720 Torr total pressure. Mixtures of borneol/H_2O_2/air and fenchol/H_2O_2/air were irradiated over periods of 3 min. Figure 5 shows an example of a chromatogram before and after irradiation of a fenchol/H_2O_2/air mixture. The only identified product for fenchol was fenchone, and for borneol, the only detected product was camphor. Figure 5 shows a collection of chromatographic peaks with values of $m/z = 166$ and 168 obtained in the product study on the reaction of fenchol with OH. This behavior was also observed in the reaction of borneol with OH. The peaks with $m/z = 166$ can be assigned to a dicarbonyl secondary product (with formula of $C_{10}H_{14}O_2$) produced by the reaction of camphor (or fenchone) with the OH radicals as was proposed by Reissell et al.[30] They proposed a collection of structures for these compounds. The peaks with $m/z = 168$ can be tentatively assigned to formation of hydroxycarbonyl compounds. Unfortunately, these compounds could not be quantified, since they are not commercially available.

Quantification has only been possible for camphor and fenchone. Reaction yields have been obtained from plots of corrected amount of camphor (or fenchone) formed versus reacted borneol (or fenchol). Figure 6 shows an example of such plots for the formation of camphor from the reactions of hydroxyl radicals and chlorine atoms with borneol. The rate coefficients obtained in this work for the reactions of camphor and fenchone with OH radicals were used to correct for secondary OH consumption of the compounds. The maximum values of the correction factors F were 1.16 and 1.09 for camphor and fenchone, respectively. The linearity of the corrected concentration versus the reacted borneol is very good for both the OH and Cl reactions. For the reaction of OH radicals with borneol an average camphor yield of (49.0 ± 1.0)% has been obtained, whereas for the reaction of OH with fenchol a yield of (60.9 ± 2.6)% has been obtained for the formation of fenchone. Cyclohexanone, camphor, and fenchone will be formed from cyclohexanol, borneol, and fenchol, respectively, via a mechanism involving abstraction of the tertiary hydrogen atom attached to the carbon bonded to the OH group. Bradley et al. have reported a yield of (55.0 ± 0.6)%

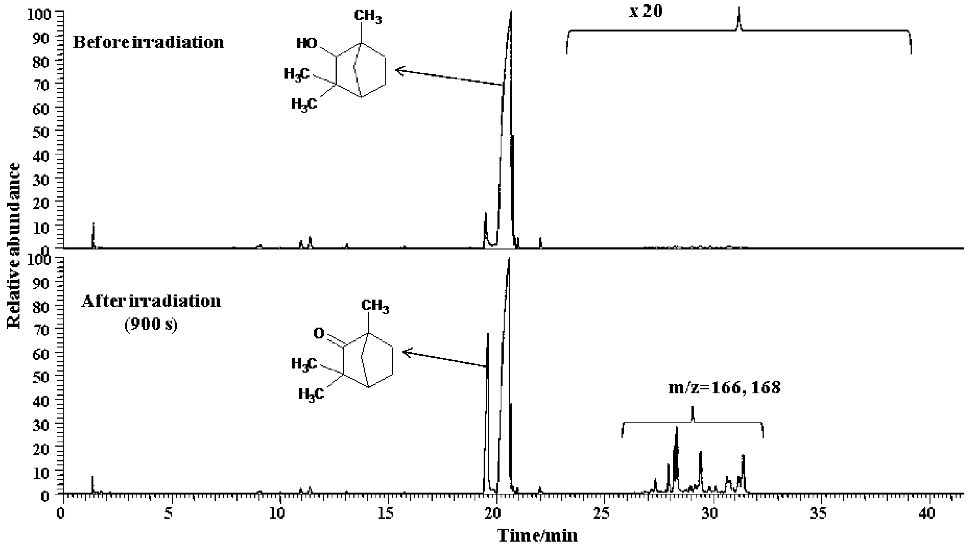


Figure 5. Gas chromatograms of samples from a fenchol/H_2O_2/air reaction mixture before and after photolysis.

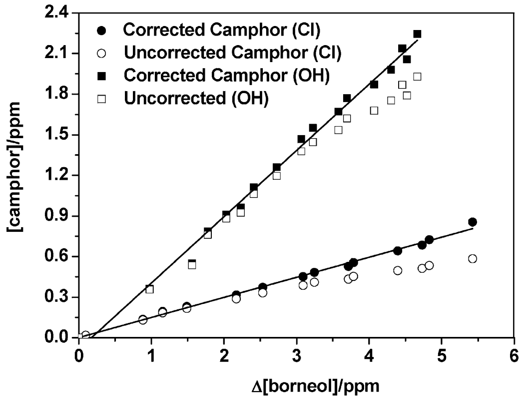


Figure 6. Examples of camphor formed in the reaction of Cl atoms and OH radicals with borneol as a function of the amount of reacted borneol with and without correction for secondary reactions using eq 5.

for cyclohexanone formation from of the reaction of OH with cyclohexanol.[31] The SAR method predicts that for cyclohexanone, camphor, and fenchone this reaction channel will account for around 58% of the total reaction, which is in good agreement with the observed carbonyl product yields.

The SAR method predicts that ~15% of the attack of OH occurs at the other tertiary hydrogen site in both borneol and fenchol; however, no experimental evidence has been reported for this pathway. Attack at the second tertiary H-atom will probably lead to ring opened products, but they have not been detected. Attack of OH at the primary hydrogens is predicted to be of only minor importance (~3.5%) whereas attack at the secondary hydrogens is predicted to be around 24%.

On the basis of the results obtained in this study and knowing the degradation pathways for VOCs in the atmosphere, mechanisms have been proposed for the reaction of radicals with borneol and fenchol. The formation of camphor and fenchone from the reaction of OH with borneol and fenchol is completely analogous to the formation of cyclohexanone from the reaction of OH radicals with cyclohexanol.

The formation of the products with *m*/*z* values of 168 and 170 can be explained by the attack of OH radicals at the $-CH_2-$ positions in camphor or borneol (fenchone or fenchol), respectively. Figure 7 shows an example of a mechanism proposed for the formation of products with *m*/*z* 168 from the reaction of borneol and OH radicals. Products with *m*/*z* 170 have not been detected which implies that the nonradical forming channels between the peroxy radicals are probably minor and that the alkoxy radical forming channel dominates.

4.3. Product Studies of Borneol and Fenchol with Cl Atoms.

Analogous to the OH, product studies were performed on the reactions of borneol and fenchol with Cl atoms in the 200 L reactor at UCLM at 298 K and 720 Torr total pressure. Mixtures of borneol/Cl_2/air and fenchol/Cl_2/air irradiated over periods of 90 s. Again, only formation of camphor and fenchone from the reactions of Cl with borneol and fenchol could be identified and quantified. The same collection of chromatographic peaks with *m*/*z* = 166 and 168 were also obtained in both cases. The yields of camphor and fenchone were determined as outlined in the OH product section, and an example is shown in Figure 6 for the formation of camphor from the reaction of Cl with borneol. The concentrations of camphor and fenchone were corrected for secondary consumption by Cl using the rate coefficients determined in this work (Table 3). The maximum correction factors were 1.16 and 1.46 for the reaction of Cl with camphor and fenchone, respectively.

Yields for the formation of camphor and fenchone from the reactions of Cl with borneol and fenchol were (13.6 ± 0.2)% and (19.6 ± 0.8)% (Table 4). These yields are somewhat higher than the yield of (9.1 ± 0.6)% for the formation of cyclohexanone from the reaction of cyclohexanol with chlorine atoms. As discussed for the analogous reactions with OH radicals, the Cl atom reactions will proceed via abstraction of the available hydrogen atoms in the molecules. The SAR method for Cl reactions predicts that for both borneol and fenchol about 11% of the reaction will proceed via abstraction of the tertiary hydrogen atom attached to the carbon atom bonded to the OH group. It is interesting to note that, as in the analogous OH reactions, the yield of camphor from the reaction of Cl with borneol is lower than the yield of fenchone from the reaction of Cl with fenchol. This can be due to steric

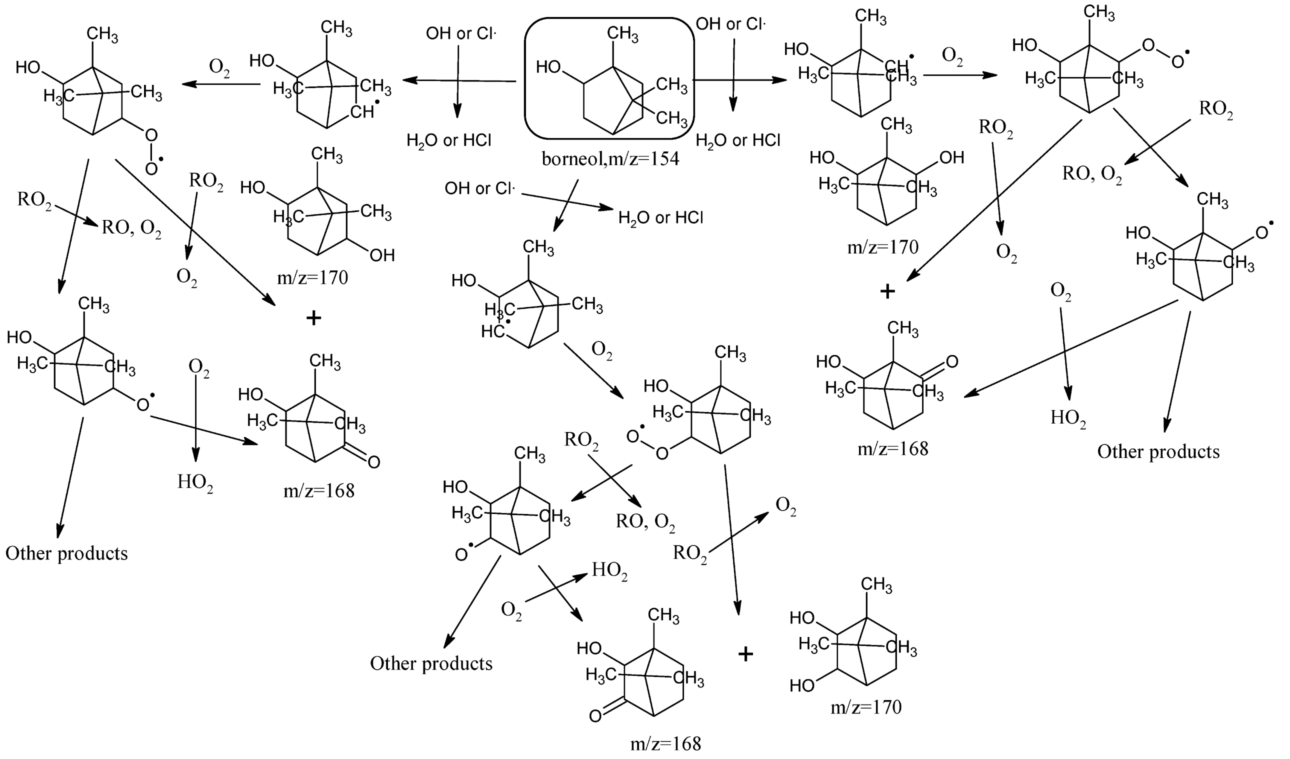


Figure 7. Proposed mechanism for the formation of products with m/z = 168 from the reactions of borneol with OH radicals or chlorine atoms.

Table 4. Primary Reaction Yields for Cyclohexanone, Camphor, and Fenchone from the Reactions of Cyclohexanol, Borneol, and Fenchol, Respectively, with Chlorine Atoms and OH Radicals[a]

compd	reaction product	Y_{OH} (%)	Y_{Cl} (%)
cyclohexanol	cyclohexanone	55.0 ± 0.6[b]	9.1 ± 0.6
borneol	camphor	49.0 ± 1.0	13.6 ± 0.2
fenchol	fenchone	60.9 ± 2.6	19.6 ± 0.8

[a] Errors are twice the standard deviation. [b] From by Bradley et al.[31]

effects or underestimation of substituent effects, as discussed for the OH reactions.

The SAR method predicts that approximately 52% of the attack of Cl occurs at the $-CH_2-$ groups and this attack can give compounds with chromatographic peaks m/z = 166 and 168. No experimental evidence for attack at the >CH− group could be found, despite the fact that SAR estimates put an importance of 10% on this reaction pathway. The peaks with m/z = 168 can be tentatively assigned to hydroxycarbonyl compounds with formula $C_{10}H_{16}O_2$ according to the mechanism proposed by Reissell et al. in 2001. The peaks with m/z = 166 can be tentatively assigned to dicarbonyl compounds with formula $C_{10}H_{14}O_2$. A mechanism based on the experimental data obtained in this study is shown in Figure 7 for the attack of Cl at the $-CH_2-$ groups in borneol. The mechanism is analogous to that proposed for reaction of the compound with OH radicals.

5. ATMOSPHERIC IMPLICATIONS

Volatile organic compounds are, in general, chemically removed from the troposphere mainly by reaction with the tropospheric oxidants such as OH, NO_3, O_3, and halogen atoms. The tropospheric lifetime (τ) of any VOC due to its reaction an oxidant X is defined according to eq 6

$$\tau = \frac{1}{k_x[X]} \tag{6}$$

where k_x is the rate coefficient of the VOC with the oxidant X (in this work Cl atoms or OH radicals) which is present in the atmosphere in a concentration [X]. For the estimation of the tropospheric lifetimes of the title compounds with respect to reaction with OH and Cl, the following average oxidant concentrations were considered: 10^6 radical cm^{-3} for OH radicals[60] and an upper limit of 10^3 atom cm^{-3} for chlorine atoms.[60,61] In marine environments, high Cl concentrations are thought to be formed shortly after sunrise as a result of the photochemistry of Cl-precursors. Spicer et al.[18] observed high concentrations of Cl_2 at night and estimated a peak Cl concentration of 1.3×10^5 atom cm^{-3}, which has also been used in the estimation of τ under these specific conditions. Table 5 shows the calculated tropospheric lifetimes of cyclohexanol and the oxygenated terpenes due to reactions with hydroxyl radicals and chlorine atoms.

The global tropospheric lifetime for reactions of OH-group-containing compounds with hydroxyl radicals is around 13 h, whereas for camphor and fenchone τ is 67 h. For the reactions with Cl, using a Cl average concentration of 10^3 atom cm^{-3}, global lifetimes of 38 days for the reactions of the alcohols and 68 days for the reactions of camphor and fenchone are calculated. Using a higher Cl atom concentration, which prevails in coastal and marine areas, the tropospheric lifetimes of the alcoholic terpenes due to the Cl-reaction are around 7 h, while they are around 12 h for camphor and fenchone. In the light of these results, it can be concluded that the main gas phase mechanism for removal of these compounds in the atmosphere will be reaction with hydroxyl radicals; never-

Table 5. Tropospheric Lifetimes of Cyclohexanol and Oxygenated Terpenes Due to Reactions with Hydroxyl Radicals and Chlorine Atoms

compd	($k_{Cl} \pm 2\sigma$) × 10^{10} (cm^3 $molecule^{-1}$ s^{-1})	($k_{OH} \pm 2\sigma$) × 10^{11} (cm^3 $molecule^{-1}$ s^{-1})	τ_{Cl}/days[a]	τ_{Cl}/h[b]	τ_{OH}/h[c]
cyclohexanol	3.21 ± 0.26	1.90 ± 0.48[d]	36	6.7	14.6
borneol	2.72 ± 0.13	2.65 ± 0.32	42	7.8	10.5
fenchol	2.93 ± 0.17	2.49 ± 0.30	39	7.3	11.2
menthol	3.40 ± 0.28	1.58 ± 0.32	34	6.3	17.6
camphor	1.59 ± 0.10	0.41 ± 0.08	73	13.4	67.8
fenchone	1.86 ± 0.29	0.42 ± 0.09	62	11.5	66.1

[a] Upper limit chlorine atom average concentration, [Cl] = 10^3 atom cm^{-3}.[60,61] [b] Coastal and marine areas at dawn, [Cl] = 1.3 × 10^5 atom cm^{-3}.[18] [c] Hydroxyl radical average concentration, [OH] = 1.0 × 10^6 radical cm^{-3}.[59] [d] From Bradley et al.[31]

theless, where the concentration of chlorine atoms can be sufficiently high, such as in coastal and marine areas,[18] reactions of the compounds with chlorine atoms can compete with the hydroxyl radical reactions.

AUTHOR INFORMATION

Corresponding Author

*Phone: +34 902 204 100. Fax: +34 902 204 130. E-mail: jose.albaladejo@uclm.es.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully thank the Spanish Ministerio de Educación y Ciencia (CGL2004-03355/CLI, CGL2007-61835/CLI, and CGL2010-19066 projects) and the Junta de Comunidades de Castilla-La Mancha (PAI-05-062 and PCI08-0123-0381 projects) for financial support of this research work. Also, A.Á.C.-V. thanks the Spanish Ministerio de Educación y Ciencia for funding his research work at the University of Wuppertal (BES-2005-10258).

REFERENCES

(1) Fuentes, J. D.; Lerdau, M.; Atkinson, R.; Baldocchi, D.; Bottenheim, J. W.; Ciccioli, P.; Lamb, B.; Geron, C.; Gu, L.; Guenther, A.; et al. *B. Am. Metereol. Soc.* **2000**, *81*, 1537−1575.

(2) Geron, C.; Owen, S.; Guenther, A.; Greenberg, J.; Rasmussen, R.; Hui Bai, J.; Li, Q.-J.; Baker, B. *Atmos. Environ.* **2006**, *40*, 1759−1773.

(3) Guenther, A.; Geron, C.; Pierce, T.; Lamb, B.; Harley, P.; Fall, R. *Atmos. Environ.* **2000**, *34*, 2205−2230.

(4) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; et al. *Geophys. Res.* **1995**, *100*, 8873−8892.

(5) Papiez, M. R.; Potosnak, M. J.; Goliff, W. S.; Guenther, A. B.; Matsunaga, S. N.; Stockwell, W. R. *Atmos. Environ.* **2009**, *43*, 4109−4123.

(6) Singer, B. C.; Coleman, B. K.; Destaillats, H.; Hodgson, A. T.; Lunden, M. M.; Weschler, C. J.; Nazaroff, W. W. *Atmos. Environ.* **2006**, *40*, 6696−6710.

(7) Baumann, M. G. D.; Batterman, S. A.; Zhang, G. Z. *For. Prod. J.* **1999**, *49*, 49−56.

(8) Steinbrecher, R.; Smiatek, G.; Köble, R.; Seufert, G.; Theloke, J.; Hauff, K.; Ciccioli, P.; Vautard, R.; Curci, G. *Atmos. Environ.* **2009**, *43*, 1380−1391.

(9) Rizzo, L. V.; Artaxo, P.; Karl, T.; Guenther, A. B.; Greenberg, J. *Atmos. Environ.* **2010**, *44*, 503−511.

(10) Hoffmann, T.; Odum, J. R.; Bowman, F.; Collins, D.; Klockow, D.; Flagan, R. C.; Seinfeld, J. H. *J. Atmos. Chem.* **1997**, *26*, 189−222.

(11) Kotzias, D.; Hjorth, J. L.; Skov, H. *Toxicol. Environ. Chem.* **1989**, *20*−*1*, 95−99.

(12) Calogirou, A.; Larsen, B. R.; Brussol, C.; Duane, M.; Kotzias, D. *Anal. Chem.* **1996**, *68*, 1499−1506.

(13) Went, F. W. *Nature* **1960**, *187*, 641−643.

(14) Trainer, M.; Williams, E. J.; Parrish, D. D.; Buhr, M. P.; Allwine, E. J.; Westberg, H. H.; Fehsenfeld, F. C.; Liu, S. C. *Nature* **1987**, *329*, 705−707.

(15) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*; Academic Press: San Diego, 2000.

(16) Elshorbany, Y.; Barnes, I.; Becker, K. H.; Kleffmann, J.; Wiesen, P. *Z. Phys. Chem.* **2010**, *224*, 967−987.

(17) Singh, H. B.; Kasting, J. F. *J. Atmos. Chem.* **1988**, *7*, 261−285.

(18) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastridge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* **1998**, *394*, 353−356.

(19) George, C.; Behnke, W.; Zetzsch, C. *ChemPhysChem* **2010**, *11*, 3059−3062.

(20) Thornton, J. A.; Kercher, J. P.; Riedel, T. P.; Wagner, N. L.; Cozic, J.; Holloway, J. S.; Dube, W. P.; Wolfe, G. M.; Quinn, P. K.; Middlebrook, A. M.; et al. *Nature* **2010**, *464*, 271−274.

(21) Ceacero-Vega, A. A.; Ballesteros, B.; Albaladejo, J.; Bejan, I.; Barnes, I. *Chem. Phys. Lett.* **2009**, *484*, 10−13.

(22) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1989**, *18*, 881−1097.

(23) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605−4638.

(24) Atkinson, R.; Arey, J. *Atmos. Environ.* **2003**, *37*, 197−219.

(25) Corchnoy, S. B.; Atkinson, R. *Environ. Sci. Technol.* **1990**, *24*, 1497−1502.

(26) Finlayson-Pitts, B. J.; Keoshian, C. J.; Buehler, B.; Ezell, A. A. *Int. J. Chem. Kinet.* **1999**, *31*, 491−499.

(27) Gill, K. J.; Hites, R. A. *J. Phys. Chem. A* **2002**, *106*, 2538−2544.

(28) Martinez, E.; Cabanas, B.; Aranda, A.; Martin, P. *Environ. Sci. Technol.* **1998**, *32*, 3730−3734.

(29) Timerghazin, Q. K.; Ariya, P. A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3981−3986.

(30) Reissell, A.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2001**, *33*, 56−63.

(31) Bradley, W. R.; Wyatt, S. E.; Wells, J. R.; Henley, M. V.; Graziano, G. M. *Int. J. Chem. Kinet.* **2001**, *33*, 108−117.

(32) Ceacero-Vega, A. A.; Ballesteros, B.; Bejan, I.; Barnes, I.; Albaladejo, J. *ChemPhysChem* **2011**, *12*, 2145−2154.

(33) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N. *J. Phys. Chem.* **1982**, *86*, 4563−4569.

(34) Baxley, J. S.; Wells, J. R. *Int. J. Chem. Kinet.* **1998**, *30*, 745−752.

(35) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int. J. Chem. Kinet.* **1995**, *27*, 453−472.

(36) Ballesteros, B.; Ceacero-Vega, A. A.; Garzón, A.; Jiménez, E.; Albaladejo, J. *J. Photochem. Photobiol. A: Chem.* **2009**, *208*, 186−194.

(37) Ballesteros, B.; Garzon, A.; Jimenez, E.; Notario, A.; Albaladejo, J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1210−1218.

(38) Arthur, C. L.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145−2148.

(39) Baker, J.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2004**, *108*, 7032−7037.

(40) Orzechowska, G. E.; Paulson, S. E. *J. Phys. Chem. A* **2005**, *109*, 5358−5365.

(41) Reisen, F.; Aschmann, S. M.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **2005**, *39*, 4447−4453.

(42) Treves, K.; Rudich, Y. *J. Phys. Chem. A* **2003**, *107*, 7809−7817.

(43) Villanueva, F.; Barnes, I.; Monedero, E.; Salgado, S.; Gómez, M. V.; Martin, P. *Atmos. Environ.* **2007**, *41*, 8796−8810.

(44) Alpendurada, M. F. *J. Chromatogr., A* **2000**, *889*, 3−14.

(45) Barnes, I.; Bastian, V.; Becker, K. H.; Fink, E. H.; Zabel, F. *Atmos. Environ.* **1982**, *16*, 545−550.

(46) Barnes, I.; Becker, K. H.; Fink, E. H.; Reimer, A.; Zabel, F.; Niki, H. *Int. J. Chem. Kinet.* **1983**, *15*, 631−645.

(47) Barnes, I.; Becker, K. H.; Zhu, T. *J. Atmos. Chem.* **1993**, *17*, 353−373.
(48) Atkinson, R. *Chem. Rev.* **1986**, *86*, 69−201.
(49) Dagaut, P.; Wallington, T. J.; Liu, R.; Kurylo, M. J. *J. Phys. Chem.* **1988**, *92*, 4375−4377.
(50) Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielsen, O. J. *Int. J. Chem. Kinet.* **1990**, *22*, 1111−1126.
(51) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685−1695.
(52) Bethel, H. L.; Atkinson, R.; Arey, J. *Int. J. Chem. Kinet.* **2001**, *33*, 310−316.
(53) Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2011**, *115*, 14452−14461.
(54) Ragains, M. L.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **1997**, *101*, 1509−1517.
(55) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1995**, *27*, 613−622.
(56) Iwasaki, E.; Matsumi, Y.; Takahashi, K.; Wallington, T. J.; Hurley, M. D.; Orlando, J. J.; Kaiser, E. W.; Calvert, J. G. *Int. J. Chem. Kinet.* **2008**, *40*, 223−229.
(57) Martinez, E.; Aranda, A.; Diaz-De-Mera, Y.; Rodriguez, A.; Rodriguez, D.; Notario, A. *J. Atmos. Chem.* **2004**, *48*, 283−299.
(58) Wallington, T. J.; Skewes, L. M.; Siegl, W. O.; Wu, C.-H.; Japar, S. M. *Int. J. Chem. Kinet.* **1988**, *20*, 867−875.
(59) Lawrence, M. G.; Jockel, P.; von Kuhlmann, R. *Atmos. Chem. Phys.* **2001**, *1*, 37−49.
(60) Singh, H. B.; Thakur, A. N.; Chen, Y. E.; Kanakidou, M. *Geophys. Res. Lett.* **1996**, *23*, 1529−1532.
(61) Wingenter, O. W.; Blake, D. R.; Blake, N. J.; Sive, B. C.; Rowland, F. S.; Atlas, E.; Flocke, F. *J. Geophys. Res., [Atmos.]* **1999**, *104*, 21819−21828.