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To cite this version:

Zahraa Dbouk, Nesrine Belhadj, Maxence Lailliau, Roland Benoit, Philippe Dagaut. On the Autoxidation of Limonene under Cool Flame Conditions: Formation of Oxygenated and Aromatic Products. 14th Asia-Pacific Conference on Combustion, The Combustion Institute, May 2023, Kaohsiung, Taiwan, R.O.C., Taiwan. hal-04385311

HAL Id: hal-04385311

https://univ-orleans.hal.science/hal-04385311

Submitted on 10 Jan 2024

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14th Asia-Pacific Conference on Combustion
Kaohsiung Exhibition Center, Kaohsiung, Taiwan
14th-18th May 2023

On the Autoxidation of Limonene under Cool Flame Conditions: Formation of Oxygenated and Aromatic Products.

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Abstract

The oxidation of limonene-O_2-N_2 mixtures and 1-methyl-cyclohexene-O_2-N_2 mixtures was conducted in a jet-stirred reactor (JSR) in the cool flame regime, fuel-lean conditions, and atmospheric pressure. Samples of the reacting mixtures were collected and analyzed by (i) on-line Fourier transform infrared spectroscopy, (ii) gas chromatography-mass spectrometry (GC-MS), and (iii) high resolution mass spectrometry after direct injection or chromatographic separation using reversed-phase ultra-high-performance liquid chromatography and +/– heated electrospray ionization and +/– atmospheric pressure chemical ionization. H/D exchange using deuterated water and reaction with 2,4-dinitrophenylhydrazine were performed to probe the presence of OH, OOH, and C=O groups in the products, respectively. A broad range of oxidation products ranging from final products to highly oxygenated products with five and more O-atoms, was detected. Besides, a range of aromatic and poly-unsaturated products were also detected. A range of tools were used to characterize and rationalize the data: Van Krevelen plots, computation of the degree of unsaturation in products.

1 Introduction

Terpenes are naturally emitted by vegetation. They represent an important fraction of volatile organic compounds present in the troposphere [1, 2]. Because of their high-energy-density, they could potentially be used as biojet fuels [3-6]. With cetane numbers of ~ 20, one could also use them as drop-in fuels for greener ground transportation. The introduction of terpenes as fuel would contribute inevitably to increased emissions into the troposphere via unburnt fuel emissions and evaporation during, e.g., refueling. Although, the kinetics of oxidation of terpenes under simulated tropospheric conditions has been extensively studied, a good knowledge of the numerous oxidation processes involved has not been reached [7]. Regarding the kinetics of combustion of this class of compounds, even less is known since, to our knowledge, only flame speeds and impact on ignition were studied [8-11]. In combustion [12-16] we consider that autoxidation of hydrocarbons (RH) produces oxygenated products such as ketohydroperoxides (KHPs) which lead to chain branching via decomposition: RH + $^{\bullet}$OH ⇄ R$^{\bullet}$ + H_2O (1); R$^{\bullet}$ + O_2 ⇄ ROO$^{\bullet}$ (2); ROO$^{\bullet}$ + HOO$^{\bullet}$ ⇄ ROOH + O_2 (3); ROO$^{\bullet}$ + RH ⇄ ROOH + R$^{\bullet}$ (4); ROO$^{\bullet}$ ⇄ $^{\bullet}$QOOH (5); ROO$^{\bullet}$ ⇄ Q (unsaturated product) + HOO$^{\bullet}$ (6); $^{\bullet}$QOOH ⇄ $^{\bullet}$OH + QO (cyclic ether) (7); $^{\bullet}$QOOH + O_2 ⇄ $^{\bullet}$OOQOOH (8); $^{\bullet}$OOQOOH ⇄ HOO$^{\bullet}$POOH (9); HOO$^{\bullet}$POOH ⇄ $^{\bullet}$OH + HOOP=O (KHPs) (10); HOOP=O ⇄ $^{\bullet}$OH + OP$^{\bullet}$O (11). Besides, the production of highly oxidized organic products in cool flames of alkanes, cycloalkanes, alcohols, aldehydes, ethers, and esters has been reported in recent studies [17-19]. This alternative oxidation pathway proceeds via an H-shift in the $^{\bullet}$OOQOOH intermediate involving a H-C group other than the H-COOH group responsible for the formation of KHPs. It opens new oxidation pathways including a third O_2 addition to HOOP$^{\bullet}$OOH yielding $^{\bullet}$OOP(OOH)$_2$. Such sequence of H-shift and O_2 addition can repeat, yielding highly oxidized products [18-20]. Besides, $^{\bullet}$QOOH can decompose to yield radicals and stable products via Reaction (7), $^{\bullet}$QOOH → carbonyl product + olefin + $^{\bullet}$OH (12), and $^{\bullet}$QOOH → $HO_2^{\bullet}$ + olefin (13). In the case of unsaturated reactant, the Waddington mechanism [21] which involves OH addition to the C=C double bond followed by O_2 addition and H-shift from the –OH group to the –OO$^{\bullet}$ peroxy group, and decomposition can occur: R-C=C-R' + $^{\bullet}$OH ⇄ R-$^{\bullet}$C-C(-R')-OH (14);$^{\bullet}$C(-R)-C(-R')-OH + O_2 ⇄ $^{\bullet}$OO-C(-R)-C(-R')-OH (15); $^{\bullet}$OO-C(-R)-C(-R')-OH ⇄ HOO-C(-R)-C(R')-O$^{\bullet}$ (16); HOO-C(-R)-C(R')-O$^{\bullet}$ → $^{\bullet}$OH + R-C=O + R'-C=O (17). Through this mechanism, the OH radical initially consumed is finally regenerated in Reaction (17). Also, as demonstrated initially in the liquid phase, the Korcek mechanism [22, 23] which transforms γ-ketohydroperoxides into a carboxylic acid and a ketone or an aldehyde can occur. The production of these chemicals via the Korcek mechanism has been suggested to happen under tropospheric conditions [24] and has also been introduced in recently proposed combustion kinetic reaction mechanisms [25, 26]. Further evidence of the occurrence of that mechanism has been presented recently [27]. Besides, the potential formation or aromatic products from the oxidation of terpenes or simple surrogates has not received much attention whereas aromatics are recognized to play a role in secondary organic aerosols formation [28].

This study aims to better characterize the autoxidation products of limonene and a simple terpene surrogate (1-methyl hexene) under cool-flame conditions and investigate the formation of aromatics there. To this end, we performed oxidation experiments in a JSR at 1 bar and oxidation products were characterized using a range of analytical techniques.

2 Methods

2.1 JSR Experiments

Experiments were conducted in a fused silica JSR (42 mL) introduced earlier [29]. As previously [30, 31] the fuels were pumped using a HPLC pump with an online degasser. The fuels were delivered to a vaporizer assembly fed with a flow of nitrogen (N_2). Fuel-N_2 and oxygen-N_2 flowed separately to the JSR to avoid premature oxidation before reaching the reactor.

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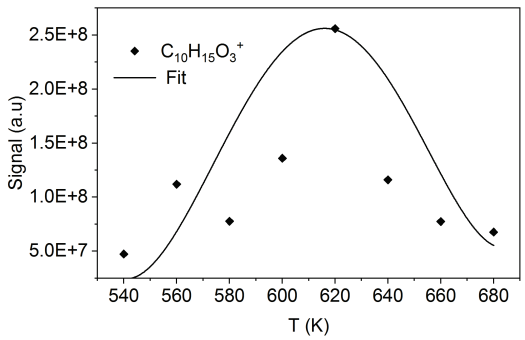
The flow rates of N_2 and O_2 were delivered by mass flow meters. Thermocouples (0.1 mm Pt-Pt/Rh-10% wires located inside a thin-wall silica tube) were moved along the vertical axis of the JSR to verify thermal homogeneity (gradients of < 1 K/cm). To observe the oxidation of the fuels in the cool-flame regime, we oxidized 1% of fuel at 1 bar, in excess of oxygen ($\varphi = 0.5$), at a residence time of 1.5 s, and over the temperature range 520-680 K.

2.2 Chemical analyzes

Gas samples were taken using a sonic probe connected to a FTIR spectrometer and a GC-MS. Standards were used for calibration. Low-temperature oxidation products were collected by bubbling gas samples for 60 min into 20 mL of UHPLC grade ≥99.9 acetonitrile maintained at 273 K. They were kept in a freezer at 258 K for future chemical analyses. We conducted flow injection analyses/heated electrospray ionization (FIA/HESI). The samples were analyzed by high-resolution mass spectrometry (HRMS). We used an Orbitrap Q-Exactive with mass accuracy <0.5 ppm RMS and mass resolution of 140,000. We performed mass calibrations in positive and negative modes by injecting +/– HESI Pierce calibration mixtures. Reverse-phase ultra-high-performance liquid chromatography (RP-UHPLC) analyses were conducted using a C_{18} analytical column (Phenomenex Luna, 1.6µm, 100 Å, 100x2.1 mm). 3 µL of samples were eluted by water-ACN mix at a flow rate of 250 µL/min (gradient 5% to 90% ACN, during 33 min). Atmospheric pressure chemical ionization (APCI) was used in positive and negative modes for the ionization of products. For determining the chemical structure of oxidation products, MS/MS analyses were conducted at a collision cell energy of 10 eV. As in previous works [32, 33] 2,4-Dinitrophenylhydrazine (2,4-DNPH) was also used to assess the presence of carbonyl compounds. 100 µL of 2,4-DNPH solution (2 g in 100 mL ACN) and 20 µL of H_3PO_4 (purity 85%) were added to 1 mL of sample. As previously [18, 19], the fast OH/OD exchange was used to assess to the presence of a hydroxyl (-OH) or hydroperoxyl (-OOH) groups in oxidation products. We added 300 µL of high-purity D_2O to 1 mL of samples and let the mix react for 20 min. We analyzed that solution using FIA-HESI-HRMS and UHPLC-APCI-HRMS.

3 Results and Discussion

A broad range of oxidation products ranging from water to highly oxygenated products, containing five and more O-atoms, was detected: $C_7H_{10}O_{4,5}$, $C_8H_{12}O_{2,4}$, $C_8H_{14}O_{2,4}$, $C_9H_{12}O$, $C_9H_{14}O_{1,3\text{-}5}$, $C_{10}H_{12}O_2$, $C_{10}H_{14}O_{1\text{-}9}$, $C_{10}H_{16}O_{2\text{-}5}$, and $C_{10}H_{18}O_6$. Figure 1 shows results obtained for KHPs and isomers and for diones which result from KHPs decomposition. As can be seen from that figure, both products peak at a temperature ~ 620 K.



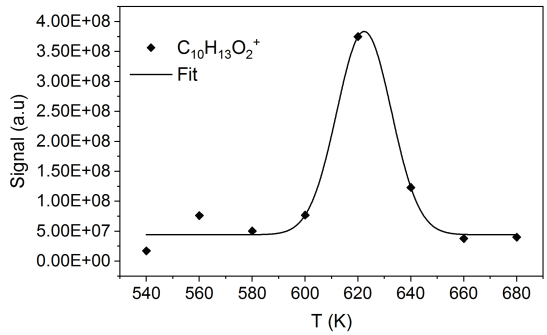


Figure 1: HRMS signal obtained for limonene products of oxidation. The data for KHPs and isomers ($C_{10}H_{14}O_3$) and diketones and isomers ($C_{10}H_{12}O_2$) were obtained via FIA and HESI (+), i.e., $C_{10}H_{15}O_3^+$ *m/z* 183.1015 and $C_{10}H_{13}O_2^+$ *m/z* 165.0910, respectively.

Carbonyl compounds from the Waddington mechanism on *exo*- and *endo*-double bonds (C=C) were observed as well as their products of further oxidation. The earlier reported [34] higher reactivity of the *endo* double bond *vs* the *exo* double bond seems to be confirmed here since higher ion signal was obtained for isoprenyl-6-oxoheptanal ($C_{10}H_{17}O_2^+$) than for limonaketone ($C_9H_{15}O^+$). Products of the Korcek mechanism (carboxylic acids and carbonyls) were also detected. Among the 18 KHPs deriving from limonene oxidation, four isomers could decompose according to the Korcek mechanism but only one will likely form a cyclic organic peroxide intermediate between the carbonyl and OOH groups which yields carbonyl compound, $C_9H_{12}O$, and formic acid, CH_2O_2 by decomposition (Fig. 2). Both products were detected in this study.

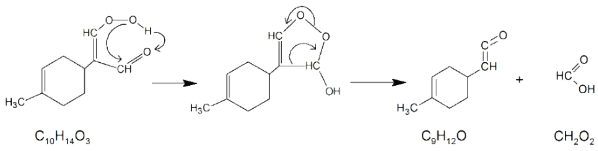


Figure 2: Korcek mechanism forming $C_9H_{12}O$ and CH_2O_2.

Based on the present identification of 1-methyl cyclohexene oxidation products, one can say the mechanisms described above occur also. Concerning the formation of aromatics, we observed by GC-MS the formation of methyl-cyclohexadienes, benzene, phenol, cresols, benzaldehyde, and toluene. Besides, vinylacetylene, 2-butene, 1,3-butadiene, cyclopentene, 1-methylcyclopentene, 1-methyl-1,3-cyclopentadiene, 5,5-dimethyl-4,3-cyclopentadiene were also detected by GC-MS.

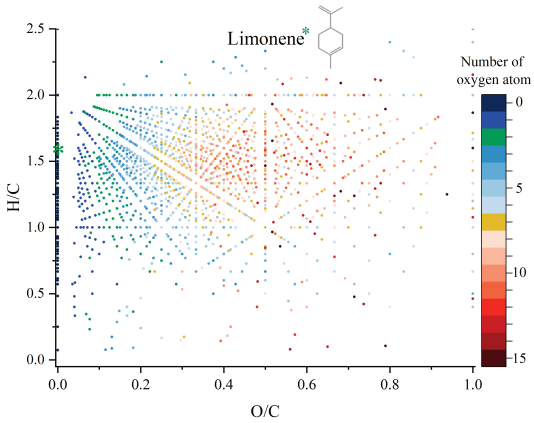


Figure 4: Van Krevelen plot for limonene oxidation. APCI+/-, FIA-HRMS (sample taken at 640 K).

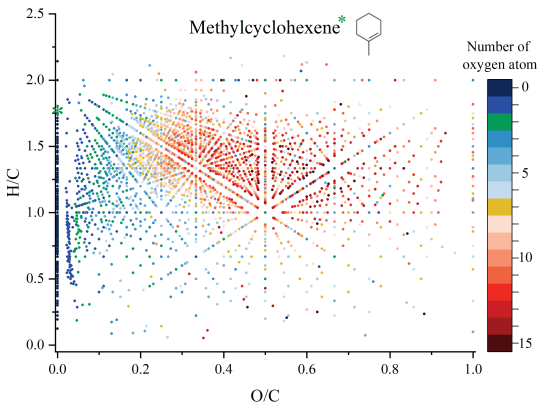


Figure 4: Van Krevelen plot 1-methylcyclohexene oxidation. These data were obtained under the following conditions: APCI+/-, FIA-HRMS (sample taken at 640 K).

The formation of C_nH_2, C_nH_4, and C_nH_6 ($n \geq 4$) isomers was observed for both fuels, but more significantly in case of 1-methylcylohexene. However, Van Krevelen plots based on HRMS data indicated the formation of aromatics and poly-unsaturated products is more important in the case of 1-methyl cyclohexene (Figs. 3 and 4). Indeed, in the space defined by $0 < O/C < 0.2$, we observed more products of oxidation and dehydrogenation from 1-methylcylohexene. For $H/C < 1$, the dedree of oxidation of products is less than for $H/C > 1$. Plotting the percentage of unsaturation versus the number of carbon atoms in the detected products (Figs. 5 and 6) confirms that in the case of 1-methyl cyclohexene higher degrees of unsaturation are reached and the products mass range extends over *m/z* 550.

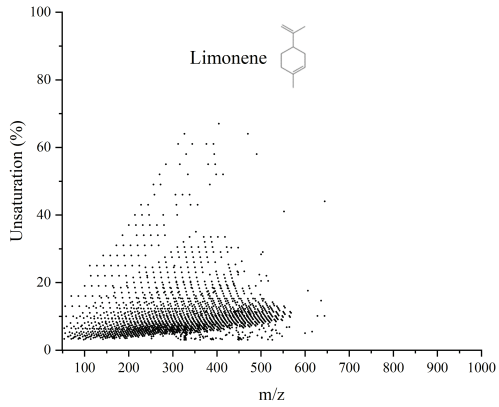


Figure 5: Variation of the degree of unsaturation.

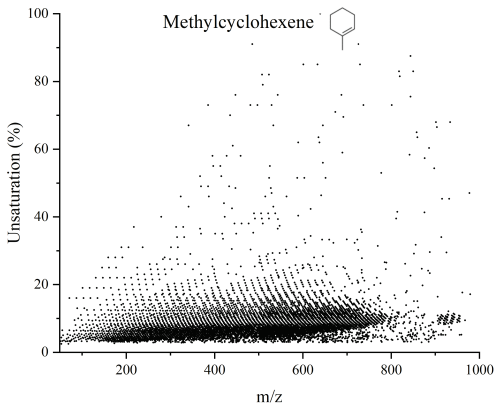


Figure 6: Variation of the degree of unsaturation.

The degree of unsaturation is defined as: (3*C+1)/(C-H/2+1) where H and C represent the number of hydrogen and carbon atoms, respectively. Below *m/z* 550, similar trends are observed. These data were obtained under the following conditions: APCI+/-, FIA-HRMS (sample taken at 640 K). This result should be taken into consideration for selecting a surrogate in future studies. Nevertheless, the present results concerning the formation of aromatics and poly-unsaturated products under cool-flame condition is rather unexpected and should be investigated under simulated atmospheric oxidation conditions since the oxidation of aromatics could play an important role in the formation of secondary organic aerosols.

4 Conclusions

This study showed that a broad range of complex oxidation products were formed. Reaction pathways include autoxidation, the Korcek mechanism, the Waddington mechanism on *exo*- and *endo*-double bonds (C=C) and autoxidation of its products. The formation of aromatic and poly-unsaturated products was observed during the autoxidation of the two fuels. The present results showed that the formation of aromatic and poly-unsaturated oxidation products is more important in the case of 1-methylcyclohexene. Then a more appropriate surrogate needs to be obtained. This work demonstrated the complexity of oxidation routes and products in the present chemical system. Our results are expected to help build detailed chemical kinetic reaction schemes for the oxidation of the terpene class of fuel. The oxidation products observed here will likely be released into the troposphere, potentially increasing the pool of VOCs which, in turn will contribute to particulates formation.

5 Acknowledgment

Financial support from CPER and EFRD (PROMESTOCK and APPROPOR-e projects), the French Ministry of Research (MESRI), the Labex CAPRYSSES (ANR-11-LABX-0006) and the Labex VOLTAIRE (ANR-10-LABX-100) is gratefully acknowledged.

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