



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

Zahraa Dbouk, Nesrine Belhadj, Maxence Lailliau, Roland Benoit, Philippe Dagaut

► 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

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Zahraa Dbouk¹, Nesrine Belhadj^{1,2}, Maxence Lailliau^{1,2}, Roland Benoit¹, Philippe Dagaut¹

Centre National de la Recherche Scientifique

¹1C Avenue de la Recherche Scientifique, Orléans, 45071, France

²Université d'Orléans

Avenue de Parc Floral, Orléans, 45067, France

Abstract

The oxidation of limonene-O₂-N₂ mixtures and 1-methylcyclohexene-O₂-N₂ 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 polyunsaturated 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 + ·OH \rightleftharpoons R' + H₂O (1); R' + O₂ \rightleftharpoons ROO· (2); ROO· + HOO· \rightleftharpoons ROOH + O₂ (3); ROO· + RH \rightleftharpoons ROOH + R· (4); ROO· \rightleftharpoons QOOH (5); ROO· \rightleftharpoons Q (unsaturated product) + HOO· (6); QOOH \rightleftharpoons ·OH + QO (cyclic ether) (7); QOOH + O₂ \rightleftharpoons OOQOOH (8); OOQOOH \rightleftharpoons HOOPOOH (9); HOOPOOH \rightleftharpoons ·OH + HOOP=O (10); HOOP=O \rightleftharpoons ·OH + OP'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 '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 O₂ addition to HOOP·OOH yielding 'OOP(OOH)₂. Such sequence of H-shift and O₂ addition can repeat, yielding highly oxidized products [18-20]. Besides, 'QOOH can decompose to yield radicals and stable products via Reaction (7), 'QOOH \rightarrow carbonyl product + olefin + ·OH (12), and 'QOOH \rightarrow HO₂· + olefin (13). In the case of unsaturated reactant, the Waddington mechanism [21] which involves OH addition to the C=C double bond followed by O₂ addition and H-shift from the -OH group to the -OO· peroxy group, and decomposition can occur: R-C=C-R' + ·OH \rightleftharpoons R-C-C(R')-OH (14); C(-R)-C(-R')-OH + O₂ \rightleftharpoons 'OO-C(-R)-C(-R')-OH (15); 'OO-C(-R)-C(-R')-OH \rightleftharpoons HOO-C(-R)-C(R')-O· (16); HOO-C(-R)-C(R')-O· \rightarrow ·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 of 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 (N₂). Fuel-N₂ and oxygen-N₂ flowed separately to the JSR to avoid premature oxidation before reaching the reactor.

*Corresponding author, Fax: +33-238-69-60-04
E-mail address: philippe.dagaut@cnrs-orleans.fr

The flow rates of N₂ and O₂ 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 ($\phi = 0.5$), 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 C₁₈ analytical column (Phenomenex Luna, 1.6 μm, 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 H₃PO₄ (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 hydroperoxy (-OOH) groups in oxidation products. We added 300 μL of high-purity D₂O 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: C₇H₁₀O_{4,5}, C₈H₁₂O_{2,4}, C₈H₁₄O_{2,4}, C₉H₁₂O, C₉H₁₄O_{1,3,5}, C₁₀H₁₂O₂, C₁₀H₁₄O_{1,9}, C₁₀H₁₆O_{2,5}, and C₁₀H₁₈O₆. 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.

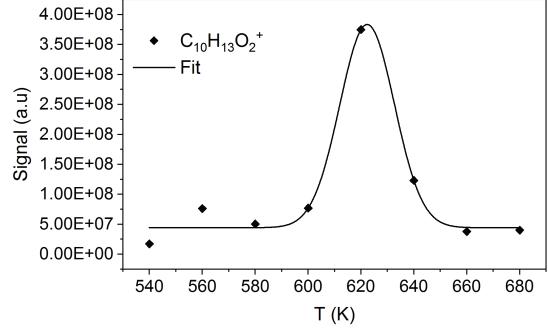
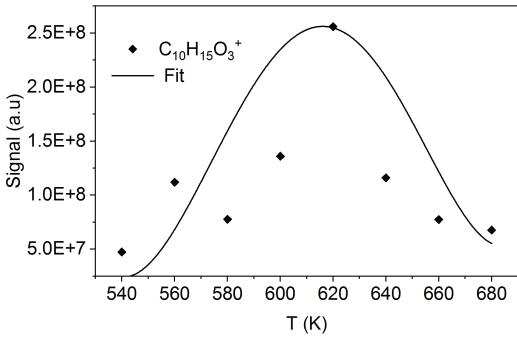


Figure 1: HRMS signal obtained for limonene products of oxidation. The data for KHPs and isomers (C₁₀H₁₄O₃) and diketones and isomers (C₁₀H₁₂O₂) were obtained via FIA and HESI (+), i.e., C₁₀H₁₅O₃⁺ *m/z* 183.1015 and C₁₀H₁₃O₂⁺ *m/z* 165.0910, respectively.

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 (C₁₀H₁₇O₂⁺) than for limonaketone (C₉H₁₅O⁺). 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, C₉H₁₂O, and formic acid, CH₂O₂ by decomposition (Fig. 2). Both products were detected in this study.

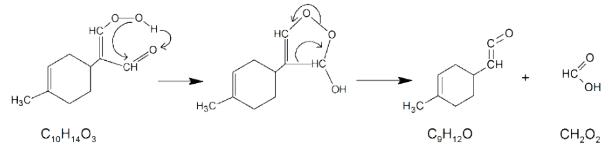


Figure 2: Korcek mechanism forming C₉H₁₂O and CH₂O₂.

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.

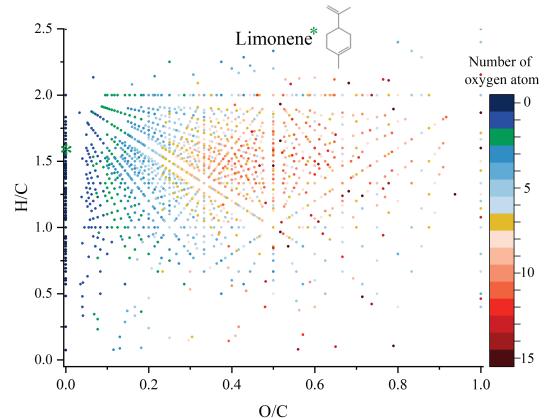


Figure 4: Van Krevelen plot for limonene oxidation. APCI+/-, FIA-HRMS (sample taken at 640 K).

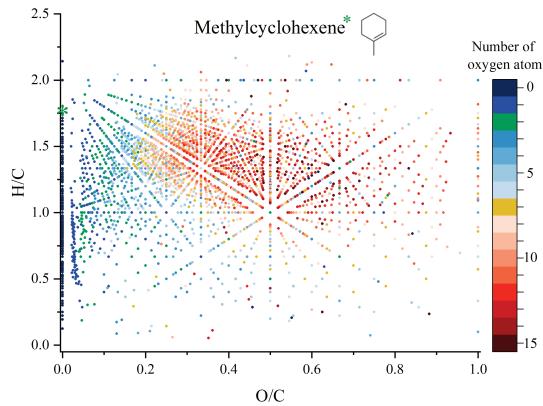


Figure 4: Van Krevelen plot 1-methylcyclohexene oxidation. These data were obtained under the following conditions: APCI $^{+/-}$, FIA-HRMS (sample taken at 640 K).

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-methylcyclohexene. 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-methylcyclohexene (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-methylcyclohexene. For $H/C < 1$, the degree 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-methylcyclohexene higher degrees of unsaturation are reached and the products mass range extends over m/z 550.

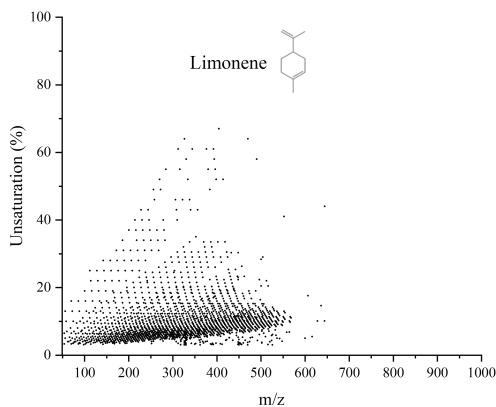


Figure 5: Variation of the degree of unsaturation.

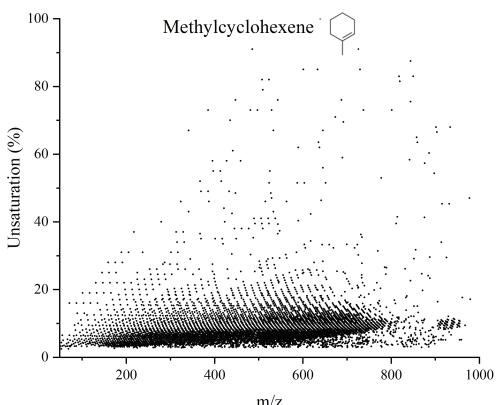


Figure 6: Variation of the degree of unsaturation.

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 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 CAPRYSES (ANR-11-LABX-0006) and the Labex VOLTAIRE (ANR-10-LABX-100) is gratefully acknowledged.

References

- [1] J. H. Seinfeld; S. N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley-Interscience, Hoboken, NJ, 2006, pp. 1-1232.
- [2] J. Llusia'; J. Penuelas, Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions, *American Journal of Botany* 87 (2000) 133-140.
- [3] M. Pourbafrani; G. Forgács; I. S. Horváth; C. Niklasson; M. J. Taherzadeh, Production of biofuels, limonene and pectin from citrus wastes, *Bioresour. Technol.* 101 (2010) 4246-4250.
- [4] H. A. Meylemans; R. L. Quintana; B. G. Harvey, Efficient conversion of pure and mixed terpene feedstocks to high density fuels, *Fuel* 97 (2012) 560-568.
- [5] B. G. Harvey; M. E. Wright; R. L. Quintana, High-Density Renewable Fuels Based on the Selective Dimerization of Pinenes, *Energy Fuels* 24 (2010) 267-273.
- [6] B. G. Harvey; W. W. Merriman; T. A. Koontz, High-Density Renewable Diesel and Jet Fuels Prepared from Multicyclic Sesquiterpanes and a 1-Hexene-Derived Synthetic Paraffinic Kerosene, *Energy Fuels* 29 (2015) 2431-2436.
- [7] T. Berndt; S. Richters; R. Kaethner; J. Voigtlaender; F. Stratmann; M. Sipilä; M. Kulmala; H. Herrmann, Gas-phase ozonolysis of cycloalkenes: Formation of highly oxidized RO₂ radicals and their reactions with NO, NO₂, SO₂, and other RO₂

- adicals, *J. Phys. Chem. A* 119 (2015) 10336.
- [8] K. Chetehouna; L. County; C. Mounaim-Rousselle; F. Halter; J.-P. Garo, Combustion Characteristics of p-Cymene Possibly Involved in Accelerating Forest Fires, *Combust. Sci. Technol.* 185 (2013) 1295-1305.
- [9] L. County; K. Chetehouna; Z. Chen; F. Halter; C. Mounaim-Rousselle; J.-P. Garo, Determination of laminar burning speeds and markstein lengths of p-cymene/air mixtures using three models, *Combust. Sci. Technol.* 186 (2014) 490-503.
- [10] L. County; K. Chetehouna; F. Halter; F. Foucher; J.-P. Garo; C. Mounaim-Rousselle, Flame speeds of alpha-pinene/air and limonene/air mixtures involved in accelerating forest fires, *Combust. Sci. Technol.* 184 (2012) 1397-1411.
- [11] J. H. Mack; V. H. Rapp; M. Broeckelmann; T. S. Lee; R. W. Dibble, Investigation of biofuels from microorganism metabolism for use as anti-knock additives, *Fuel* 117 (2014) 939-943.
- [12] S. W. Benson, The kinetics and thermochemistry of chemical oxidation with application to combustion and flames, *Prog. Energy Combust. Sci.* 7 (1981) 125-134.
- [13] R. A. Cox; J. A. Cole, Chemical aspects of the autoignition of hydrocarbon-air mixtures, *Combust. Flame* 60 (1985) 109-123.
- [14] C. Morley, A Fundamentally Based Correlation Between Alkane Structure and Octane Number, *Combust. Sci. Technol.* 55 (1987) 115-123.
- [15] Z. D. Wang; O. Herbinet; N. Hansen; F. Battin-Leclerc, Exploring hydroperoxides in combustion: History, recent advances and perspectives, *Prog. Energy Combust. Sci.* 73 (2019) 132-181.
- [16] J. Zador; C. A. Taatjes; R. X. Fernandes, Kinetics of elementary reactions in low-temperature autoignition chemistry, *Prog. Energy Combust. Sci.* 37 (2011) 371-421.
- [17] Z. D. Wang; B. J. Chen; K. Moshammer; D. M. Popolan-Vaida; S. Sioud; V. S. B. Shankar; D. Vuilleumier; T. Tao; L. Ruwe; E. Brauer; N. Hansen; P. Dagaut; K. Kohse-Höinghaus; M. A. Raji; S. M. Sarathy, n-Heptane cool flame chemistry: Unraveling intermediate species measured in a stirred reactor and motored engine, *Combust. Flame* 187 (2018) 199-216.
- [18] Z. Wang; D. M. Popolan-Vaida; B. Chen; K. Moshammer; S. Y. Mohamed; H. Wang; S. Sioud; M. A. Raji; K. Kohse-Höinghaus; N. Hansen; P. Dagaut; S. R. Leone; S. M. Sarathy, Unraveling the structure and chemical mechanisms of highly oxygenated intermediates in oxidation of organic compounds, *Proceedings of the National Academy of Sciences* 114 (2017) 13102-13107.
- [19] N. Belhadj; R. Benoit; P. Dagaut; M. Lailliau; Z. Serinyel; G. Dayma; F. Khaled; B. Moreau; F. Foucher, Oxidation of di-n-butyl ether: Experimental characterization of low-temperature products in JSR and RCM, *Combust. Flame* 222 (2020) 133-144.
- [20] N. Belhadj; R. Benoit; P. Dagaut; M. Lailliau; Z. Serinyel; G. Dayma, Oxidation of di-n-propyl ether: Characterization of low-temperature products, *Proc. Combust. Inst.* 38 (2021) 337-344.
- [21] D. J. M. Ray; A. Redfearn; D. J. Waddington, Gas-phase oxidation of alkenes: decomposition of hydroxy-substituted peroxy radicals, *Journal of the Chemical Society, Perkin Transactions 2* (1973) 540-543.
- [22] R. K. Jensen; S. Korcek; L. R. Mahoney; M. Zinbo, Liquid-phase autoxidation of organic-compounds at elevated-temperatures .2. Kinetics and mechanisms of the formation of cleavage products in normal-hexadecane autoxidation, *J. Am. Chem. Soc.* 103 (1981) 1742-1749.
- [23] A. Jalan; I. M. Alecu; R. Meana-Paneda; J. Aguilera-Iparraguirre; K. R. Yang; S. S. Merchant; D. G. Truhlar; W. H. Green, New Pathways for Formation of Acids and Carbonyl Products in Low-Temperature Oxidation: The Korcek Decomposition of gamma-Ketohydroperoxides, *J. Am. Chem. Soc.* 135 (2013) 11100-11114.
- [24] A. Mutzel; L. Poulain; T. Berndt; Y. Iinuma; M. Rodigast; O. Böge; S. Richters; G. Spindler; M. Sipilä; T. Jokinen; M. Kulmala; H. Herrmann, Highly Oxidized Multifunctional Organic Compounds Observed in Tropospheric Particles: A Field and Laboratory Study, *Environmental Science & Technology* 49 (2015) 7754-7761.
- [25] E. Ranzi; C. Cavallotti; A. Cuoci; A. Frassoldati; M. Pelucchi; T. Faravelli, New reaction classes in the kinetic modeling of low temperature oxidation of n-alkanes, *Combust. Flame* 162 (2015) 1679-1691.
- [26] C. Xie; M. Lailliau; G. Issayev; Q. Xu; W. Chen; P. Dagaut; A. Farooq; S. M. Sarathy; L. Wei; Z. Wang, Revisiting low temperature oxidation chemistry of n-heptane, *Combust. Flame* 242 (2022) 112177.
- [27] D. M. Popolan-Vaida; A. J. Eskola; B. Rotavera; J. F. Lockyear; Z. D. Wang; S. M. Sarathy; R. L. Caravan; J. Zador; L. Sheps; A. Lucassen; K. Moshammer; P. Dagaut; D. L. Osborn; N. Hansen; S. R. Leone; C. A. Taatjes, Formation of Organic Acids and Carbonyl Compounds in n-Butane Oxidation via gamma-Ketohydroperoxide Decomposition, *Angewandte Chemie-International Edition* 61 (2022) 9168-9168.
- [28] M. Li; J. Li; Y. Zhu; J. Chen; M. O. Andreae; U. Pöschl; H. Su; M. Kulmala; C. Chen; Y. Cheng; J. Zhao, Highly oxygenated organic molecules with high unsaturation formed upon photochemical aging of soot, *Chem* 8 (2022) 2688-2699.
- [29] P. Dagaut; M. Cathonet; J. P. Rouan; R. Foulquier; A. Quilgars; J. C. Boettner; F. Gaillard; H. James, A Jet-Stirred Reactor for Kinetic-Studies of Homogeneous Gas-Phase Reactions at Pressures up to 10-Atmospheres (~ 1 MPa), *Journal of Physics E-Scientific Instruments* 19 (1986) 207-209.
- [30] S. Thion; C. Togbe; Z. Serinyel; G. Dayma; P. Dagaut, A chemical kinetic study of the oxidation of dibutyl-ether in a jet-stirred reactor, *Combust. Flame* 185 (2017) 4-15.
- [31] G. Dayma; C. Togbe; P. Dagaut, Experimental and Detailed Kinetic Modeling Study of Isoamyl Alcohol (Isopentanol) Oxidation in a Jet-Stirred Reactor at Elevated Pressure, *Energy Fuels* 25 (2011) 4986-4998.
- [32] N. Belhadj; M. Lailliau; R. Benoit; P. Dagaut, Experimental and kinetic modeling study of n-hexane oxidation. Detection of complex low-temperature products using high-resolution mass spectrometry, *Combust. Flame* 233 (2021) 111581.
- [33] N. Belhadj; M. Lailliau; R. Benoit; P. Dagaut, Towards a Comprehensive Characterization of the Low-Temperature Autoxidation of Di-n-Butyl Ether, *Molecules* 26 (2021) 7174.
- [34] B. Witkowski; M. Al-sharafi; T. Gierczak, Kinetics of Limonene Secondary Organic Aerosol Oxidation in the Aqueous Phase, *Environmental Science & Technology* 52 (2018) 11583-11590.