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Unraveling the Complex Oxidation Processes Occurring Under Cool Flame Conditions.

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ABSTRACT

We oxidized limonene and α-pinene with O_2-N_2 mixtures in a jet-stirred reactor at 1 bar, in the cool flame regime, and fuel-lean conditions. Samples of the reacting mixtures were collected, dissolved in acetonitrile, and analyzed by high-resolution mass spectrometry H/D exchange using D_2O and reaction with 2,4-dinitrophenylhydrazine used for probing the presence in the products of hydroxy/hydroperoxy, and carbonyl groups, respectively. A huge set of oxidation products, including highly oxygenates with ≥ 5 O-atoms, was observed. Aromatic and polyunsaturated products were detected.

1. Introduction

The formation of ketohydroperoxides and highly oxygenated molecules (HOMs)[1-3] is of interest for getting a better understanding of the mechanisms of both combustion and the formation of atmospheric secondary organic aerosols (SOAs) in the troposphere produced via an intricate interaction of sunlight and volatile organic compounds (VOCs) from vegetation (e.g., terpenes) and human activities. Such chemicals are relatively unstable and difficult to analyze. In order to get more insights into oxidation mechanisms, new experiments are needed. Because terpenes represent also potential renewable transportation fuels[4], we studied the low-temperature oxidation of limonene and α-pinene at constant residence time and variable temperature in a jet-stirred reactor (JSR). The experimental conditions were selected to favor the production of ketohydroperoxides. Atmospheric pressure chemical ionization (APCI) or heated electrospray ionization (HESI)– mass spectrometry (Orbitrap) were used to probe the formation of ketohydroperoxides, HOMs, and the products of the so-called Korcek mechanism through which chain branching ketohydroperoxides [5] are transformed into stable products.

2. Method

The experiments were performed in a fused-silica JSR presented earlier [6, 7]. A 40 mm o.d. spherical sphere (35 cm^3 internal volume) equipped with 4 injectors having nozzles of 1 mm i.d., for the admission of the gases achieving the stirring, constitutes the JSR. It is located inside a temperature-controlled oven of c.a.1.5 kW, surrounded by insulating material. The JSR operates at atmospheric pressure. N_2 and O_2 flow rates were measured and regulated by thermal mass-flow controllers. The liquid fuels were delivered by a HPLC pump and vaporized before injection into the reactor. A good thermal homogeneity along the whole vertical axis of the JSR was obtained in the experiments. The temperature was measured using a Pt/Pt-Rh10% thermocouple of 0.1 mm diameter located inside a thin-wall fused-silica tube (<0.5mm), which prevents catalytic reactions on the metal wires. The high degree of dilution used in these experiments yielded a small temperature rise in the JSR. Samples of the reacting mixture were taken using a quartz probe connected to a cool acetonitrile tank. The resulting solution was stored in a freezer at ~220 K for further analyses using soft ionization and high-resolution mass spectrometry. Positive ($M + H^+ \rightarrow MH^+$) and negative ($MH \rightarrow M_{-H}^-$) were used for products identification.

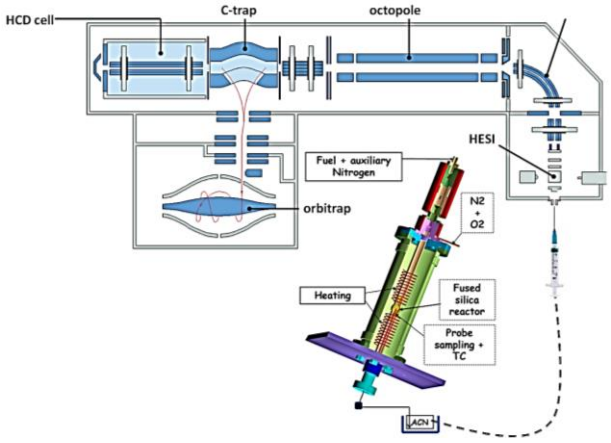

Fig. 1 Overview of the experimental setup.

Hydrogen–Deuterium exchange reactions involving the addition of D_2O in the samples were used to confirm the presence of –OH or –OOH groups in the products.

3. Results and Discussion

Experiments were performed at 1 bar for an equivalence ratio of 0.5, an initial concentration of fuels of 10,000 ppm, and a fixed residence time τ = 1.5 s. The temperature in the JSR was varied from 520 to 680 K.

The formation of ketohydroperoxides and highly oxygenated compounds resulting from third O_2 addition on the fuels radicals (R) was observed. The reactions proceed through:

$R + O_2 \leftrightarrows RO_2$

$RO_2 \leftrightarrows QOOH$

$QOOH + O_2 \leftrightarrows OOQOOH$

$OOQOOH \leftrightarrows HOOQ'OOH$ followed by the formation of the hydroxyl radical and a ketohydroperoxide:

$HOOQ'OOH \rightarrow HOOQ'O + OH$

Dihydroperoxides can also react with molecular oxygen (3rd O_2 addition):

$HOOQ'OOH + O_2 \leftrightarrows (HOO)_2Q'OO$

$(HOO)_2Q'OO \leftrightarrows (HOO)_2POOH$

$(HOO)_2POOH \rightarrow OH + (HOO)_2P{=}O$

The reaction can also proceed through a 4th O_2 addition:

$(HOO)_2POOH + O_2 \rightarrow (HOO)_3POO$

$(HOO)_3POO \leftrightarrows (HOO)_3P'OOH$

$(HOO)_3P'OOH \rightarrow OH + (HOO)_3P'{=}O$

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Products of the Korcek mechanism (carboxylic acids and carbonyls) were also detected. Among the 18 KHPs deriving from limonene oxidation, four isomers could decompose via the Korcek mechanism. But, only one isomer can possibly yield a cyclic intermediate peroxide linking the carbonyl and OOH groups which yields a carbonyl compound, $C_9H_{12}O$, and formic acid, CH_2O_2 by decomposition (Fig. 2). Both products were detected.

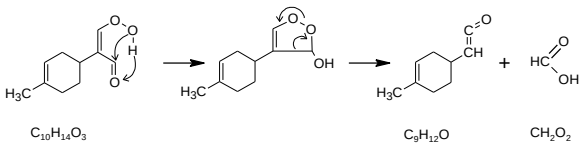

Fig. 2 Korcek mechanism during limonene oxidation.

The formation of C_nH_2, C_nH_4, and C_nH_6 ($n \geq 4$) isomers was observed for both terpene fuels on line 4 with O/C = 0 in Van Krevelen plots using HESI+/– FIA-HRMS data (Figs. 3-4); the position of the fuels is shown as a circle.

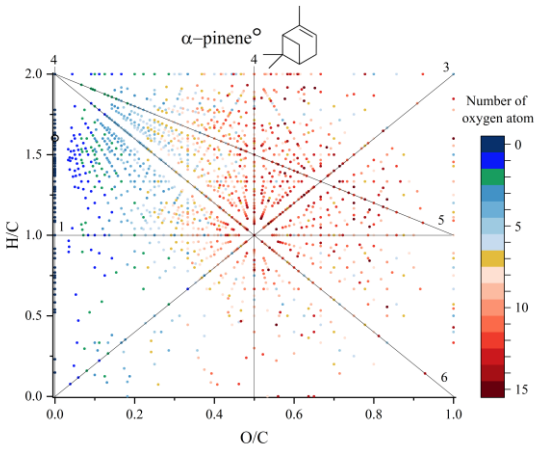

Fig. 3 Van Krevelen plot for α-pinene oxidation products. HESI+/–, FIA-HRMS (sample taken at 640 K). Lines indicate 1: oxidation, 2: carbonylation, 3: hydration, 4: dehydrogenation, 5: carboxylation, or reverse processes.

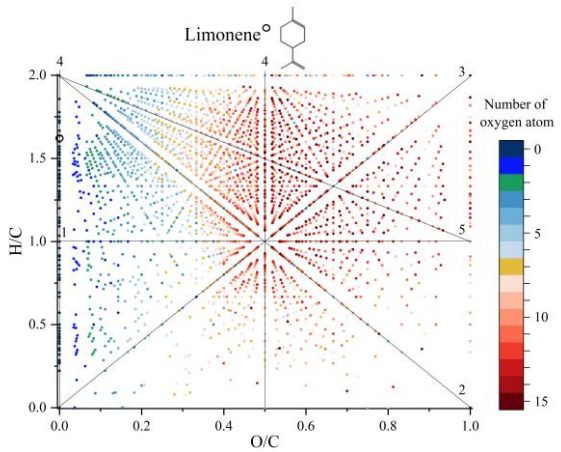

Fig. 4 Van Krevelen plot for limonene oxidation products. (sample taken at 640 K).

These plots indicated the formation of aromatics (H/C < 0.7 and O/C = 0) and polyunsaturated products. In the space defined by 0 < O/C < 0.2, we observed products of oxidation (line 1) and dehydrogenation (line 4). 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 C-atoms in the detected products confirms that high degrees of unsaturation are reached and that the products mass range extends over m/z 550.

4. Concluding Remarks

A large set of complex products of oxidation in a JSR of limonene and α-pinene were detected at 1 bar and fuel-lean conditions. The formation of polyunsaturated and aromatic products was observed during the autoxidation of the two fuels using high-resolution mass spectrometry. It was observed that under the present experimental conditions, the oxidation of limonene forms significantly more high molecular weight products than α-pinene.

Acknowledgements

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