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Proceedings

On the Formation of Aromatics From Cyclic Hydrocarbon Fuels Under Cool Flame Conditions: From Methylcyclohexene to Terpenes.

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ABSTRACT

We oxidized three isomers of methylcyclohexene with O₂-N₂ mixtures in a jet-stirred reactor at 10 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. A huge set of oxidation products, including highly oxygenated chemicals, aromatic and polyunsaturated products was obtained.

1. Introduction

Because terpenes are potential renewable transportation fuels [1], it is important to investigate their kinetics of oxidation. However, since such chemicals are rather complex (Fig. 1), the study of the oxidation of simpler model fuels such as substituted cyclohexenes could be useful [2, 3].

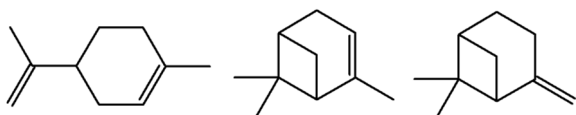


Fig. 1 Chemical structure of limonene, α -pinene, and β -pinene (from left to right).

Therefore, in order to get more insights into oxidation mechanisms, new experiments were performed. In this work, we studied the low-temperature oxidation of three methylcyclohexene isomers (Fig. 2) at constant residence time and variable temperature in a jet-stirred reactor (JSR).

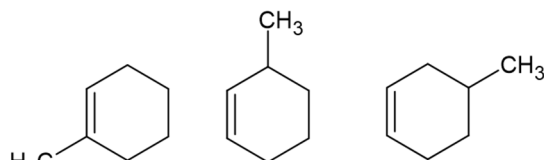


Fig. 2 Cyclohexene isomers studied here.

The experimental results were compared to those obtained for the oxidation of limonene. Atmospheric pressure chemical ionization (APCI) or heated electrospray ionization (HESI)-mass spectrometry (Orbitrap) were used to probe the formation of aromatic hydrocarbons. Besides, highly oxygenated products were also detected.

2. Method

The experiments were performed in a fused-silica JSR presented earlier [4, 5]. A 40 mm o.d. spherical sphere (35 cm³ 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 1 to 10 bar. N₂ and O₂ 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 (Fig. 3). The resulting solution was stored in a freezer at ~220 K for further analyses using soft ionization and high-resolution mass spectrometry (HRMS)[6-8]. Positive ($M + H^+ \rightarrow MH^+$) and negative ($MH \rightarrow M_{-H}^-$) were used for products identification.

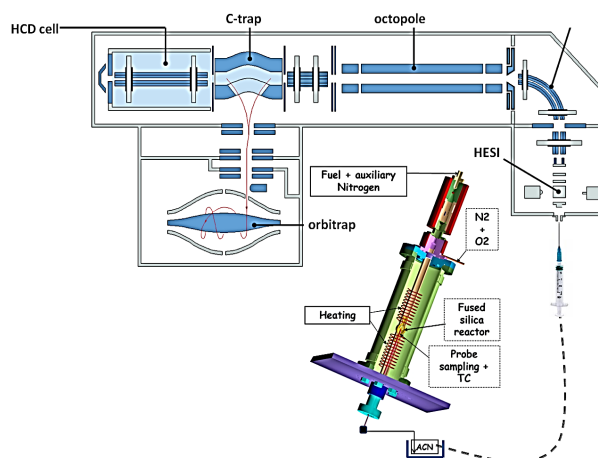


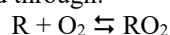
Fig. 3 Overview of the experimental setup.

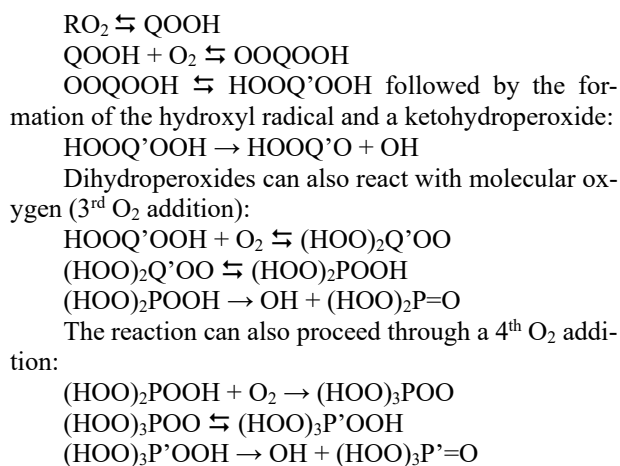
Hydrogen-deuterium exchange reactions via the addition of D₂O in the samples were used to confirm the presence of -OH or -OOH groups in the products.

3. Results and Discussion

Experiments were performed at 1-10 bar for an equivalence ratio of 0.5, an initial concentration of fuels of 3,000 to 10,000 ppm, and a fixed residence time $\tau = 1.5$ to 2 s. The temperature in the JSR was varied from 520 to 1150 K.

The formation of ketohydroperoxides and highly oxygenated compounds resulting from third O₂ addition on the fuels radicals (R) was observed. The reactions proceeded through:





Van Krevelen plots using HRMS data were used to compare products formation during the oxidation of methylcyclohexene isomers (Fig. 4) and limonene (Fig. 5).

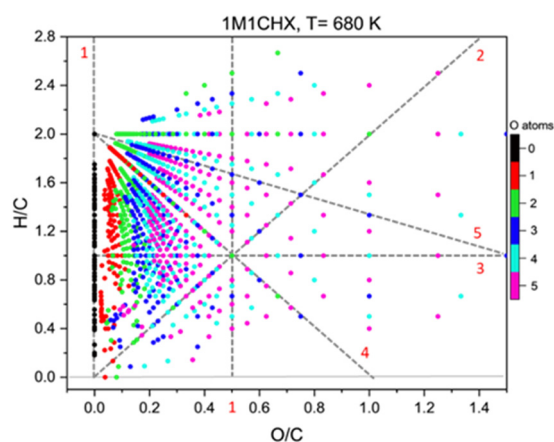


Fig. 4 Van Krevelen plot for 1-methylcyclohexene oxidation products using HRMS data (sample taken at 680 K). Lines indicate 1: dehydrogenation, 2: dehydrogenation, 3: oxidation, 4: carbonylation, 5: carboxylation, or reverse processes.

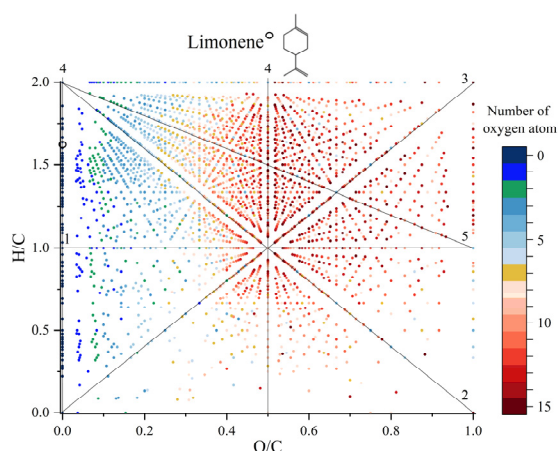


Fig. 5 Van Krevelen plot for limonene oxidation products. (sample taken at 640 K).

Because limonene is a larger fuel (C₁₀) compared to 1-methylcyclohexene (C₇), one can expect the formation of more complex and more oxygenated products. This is what was observed here (Figs. 4-5). Besides, 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 3) and dehydrogenation (line 1). For H/C < 1, the degree of oxidation of products is less than for H/C > 1. We also computed the aromaticity index:

$$\text{AI} = (1 + C - 0.5 \times O - 0.5 \times H) / (C - 0.5 \times O)$$

In this equation, *C*, *H*, and *O* represent the number of carbon, hydrogen, and oxygen atoms, respectively, in the chemical formulas.

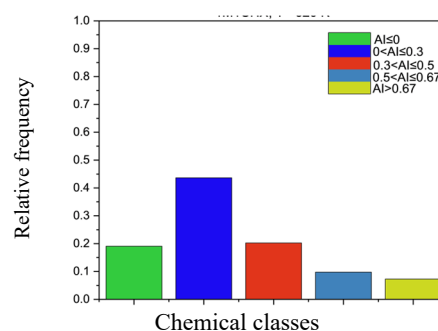


Fig. 6 Relative frequencies of chemical classes observed during the oxidation of 1-methylcyclohexane at 620 K.

In Figs 6-7, we defined several chemical classes: aliphatic compounds ($A \leq 0$), olefinic products and naphthenic compounds ($0 < AI < 0.3$) including the fuel which have an AI of 0.3, highly unsaturated compounds ($0.3 < AI \leq 0.5$), aromatics ($0.5 < AI \leq 0.67$), and polyaromatics ($0.67 < AI$). As can be seen from Fig. 6, a significant fraction of aromatic and polyaromatic hydrocarbons are present in the products. Interestingly, a similar trend was observed in the case of the oxidation of limonene (Fig. 7)

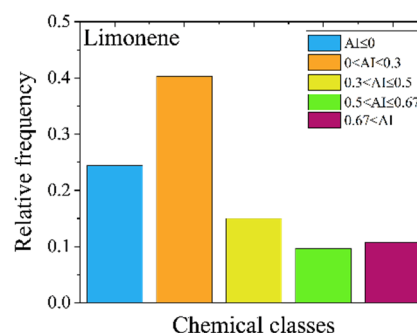


Fig. 7 Relative frequencies of chemical classes observed during the oxidation of 1-limonene at 620 K.

4. Concluding Remarks

A large set of complex products of oxidation of limonene and methylcyclohexenes was detected in a JSR under cool-flame and fuel-lean conditions. The formation of polyunsaturated and aromatic products was observed

during the autoxidation of the fuels using high-resolution mass spectrometry. It was also observed that under the present experimental conditions, the oxidation of limonene forms significantly more high molecular weight products than the methylcyclohexene isomers.

Acknowledgements

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