

Investigation of the low temperature oxidation of hexanal in a jet-stirred reactor

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Introduction

Aldehydes are important intermediates formed in the low-temperature oxidation of hydrocarbons and novel biofuels such as long chain alcohols for example. Their oxidation chemistry is of crucial importance for a good prediction of this class of pollutants formed during combustion processes [1]. Following our previous work about the oxidation of 1-hexanol presented at ECM 2015 [2], it was decided to go deeper in the understanding of the chemistry of this long chain alcohol through the investigation of the oxidation of hexanal which was the main intermediate (except CO) observed at low-temperature during the 1-hexanol study. Another important intermediate observed during the low-temperature oxidation of 1-hexanol was hexanoic acid. Again this class of compounds has received little attention and its route of formation is still not fully very certain. The goal of the present study was to investigate the oxidation of neat hexanal in a jet-stirred reactor with detailed species quantification to obtain valuable information for a better understanding of the chemistry of this class of compounds.

Experimental results

The oxidation of hexanal was performed in a jet stirred reactor (a type of perfectly stirred reactor). This reactor has often been used for numerous gas phase kinetic studies of hydrocarbons and oxygenated compounds oxidation. Details about this reactor can be found in [3]. Experiments were performed at a constant pressure of 1.067 bar, at a residence time of 2 seconds, at temperatures ranging from 500 to 1100 K, and at three equivalent ratios: 0.5, 1 and 2. The fuel was diluted in helium in order to have a hexanal mole fraction of 0.005. The fuel was provided by Sigma-Aldrich (purity of 99%). Helium and oxygen were provided by Messer (purities of 99.99% and 99.999%, respectively). Reaction products were quantified using gas chromatography. The procedure used for the quantification can be found in [2].

The fuel mole fractions profiles obtained for hexanal are completely different from that obtained for 1-hexanol as it can be seen in Figure 1. As an example, some reactivity is already observed from 475 K for hexanal (Figure 1a), whereas the consumption of 1-hexanol was only observed from 600 K (Figure 1b). Another important difference is the presence of a strong negative temperature coefficient (NTC) behavior for hexanal whereas no NTC was observed for 1-hexanol. This is the evidence that the two types of fuel react in very different ways.

Many reaction products were identified and quantified during this study. Among these species we can find usual families of combustion products (small olefins, aldehydes and ketones), as well as some oxygenated C₆ species with the same skeleton as the reactant

(Figure 2). These species are hexanoic acid (with a selectivity of about 20% at 625 K) and 5-ethyl-dihydrofuranone (selectivity of 2% at 625 K). As for 1-hexanol, hexanoic acid is the main reaction product at low-temperature (except CO). These two species were also present during the oxidation of 1-hexanol.

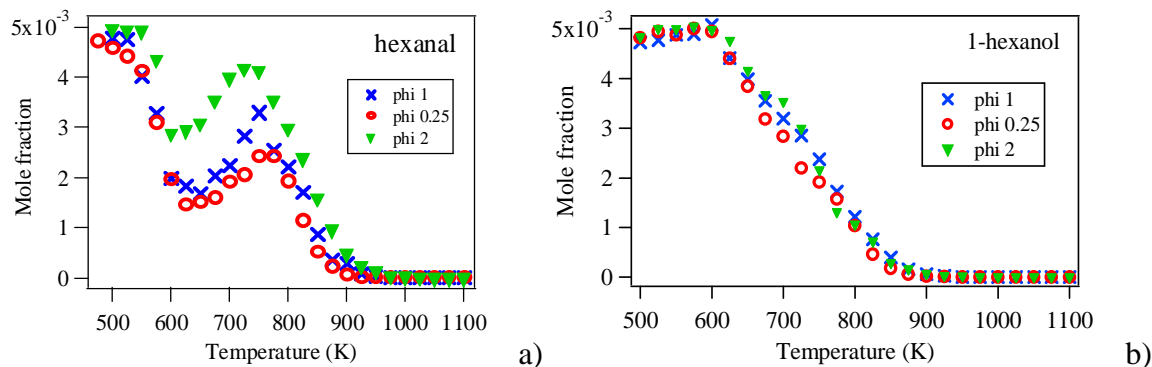


Figure 1: Mole fractions of hexanal (a) and 1-hexanol (b) as a function of the temperature and under similar conditions ($x_{fuel} = 0.005$, $P = 106.7$ kPa, $\tau = 2$ s, $\phi = 0.5, 1$ & 2).



Figure 2: Chemical structures of oxygenated C₆ species with the same skeleton as the reactant observed in the oxidation of hexanal.

Conclusion and perspectives

The oxidation of hexanal revealed interesting information about the chemistry occurring at low-temperature. An important reactivity was observed from 475 K and large amounts of hexanoic acid were formed. The next challenge will be the development of a detailed kinetic model for the oxidation of hexanal by taking into account the specific chemistry of the carbonyl group and the possible routes to hexanoic acid.

References

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