

Oxidation of C₃ and n-C₄ aldehydes at low temperatures

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Abstract

Due to the increasing interest in the use of biofuels such as alcohols mainly in blend with fossil fuels, it is of great importance to assess the combustion characteristics of intermediate species such as aldehydes, both in the high and in the low temperature combustion regime. Starting from the high temperature mechanism for n-C₃-C₅ aldehydes recently developed at Politecnico di Milano-POLIMI (*Combust. Flame* 2015, 162 (2), 265-286), and from the low temperature kinetics of acetaldehyde, a detailed kinetic mechanism has been developed to describe the low temperature oxidation of propanal and n-butanal. The validation has been carried out by comparison with recently published species measurements in isothermal Jet Stirred Reactors by Veloo et al. (*Proc. Combust. Inst.* 2013, 34 (1), 599-606; *Combust. Flame* 2013, 160 (9), 1609-1626) at T=500-1100 K, p=10 atm and φ=0.3, 0.5, 1.0 and 2.0. Aldehydes reactivity is largely dominated by H-abstraction from the carbonyl site (α) leading to the formation of R_n•C=O radical, which rapidly decomposes to form CO and the corresponding •R_n alkyl radical. Therefore, the low temperature oxidation of R_nCHO aldehydes is strictly related to the low temperature oxidation of the corresponding R_nH alkane. The scarcity of experimental measurements at engine relevant conditions in other facilities (shock tubes, rapid compression machines) preclude any wide range validations of the present model. Reduction of the number of species in the aldehydes sub-mechanism through lumping will follow in a future study.

Introduction

Biofuels from renewable sources have the potential to play a major role in meeting energy demand in transportation systems. Despite production issues and higher production costs compared to fossil fuels, biofuels offer opportunities to extend the petroleum era, as blending agents with fossil fuels or as a complete replacement [1]. In particular alcohols with various molecular structures (i.e., carbon number and substitution: ethanol, butanol isomers, pentanols) can be used in today's SI and CI engines with minor modifications to the engine design [2]. Despite the general reduction of CO, NOx and PM emissions an increase in the emissions of harmful carbonyl compounds such as aldehydes and ketones is observed. As deeply investigated in the literature and clearly summarized in a recent review paper by Mani Sarathy et al. [2], the presence of the hydroxyl moiety in alcohol molecules,

causes the reactive path proceeding towards aldehydes formation to be of key importance both in the high and the low temperatures conditions. For this reasons exploring the viability of biofuels such as alcohols in terms of combustion properties and pollutants emissions, requires a detailed knowledge of aldehydes oxidation kinetics. Starting from the high temperature mechanism for *n*-C₃-C₅ aldehydes, recently developed at Politecnico di Milano [3] and from the low temperature kinetics of acetaldehyde, a detailed kinetic mechanism has been developed to describe the low temperature oxidation of propanal and *n*-butanal. Model results are compared with speciation data in Jet Stirred Reactor as measured by Veloo et al. [4,5]. This data represents the only experimental measurements for aldehydes oxidation at low temperatures in the literature at present.

Kinetic Mechanism

Aldehydes are consumed via hydrogen abstraction from the weakly bound aldehydic R_nH-C=O site (α). Figure 1 shows relative importance of the available abstraction positions at T=650K (0.15% fuel in nitrogen, $\Phi=0.5$) for propanal and *n*-butanal, according to the rate constants discussed by Pelucchi et al. [3].

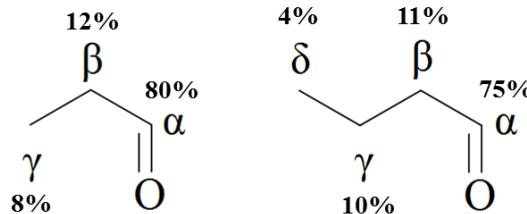


Figure 1. Relative importance of H-abstraction channels for propanal (left) and *n*-butanal (right) at T=650 K.

The R_n•C=O radical (α) is rapidly decomposed to form CO and R_n alkyl radical, according to the rate constant $k=5.78 \cdot 10^{14} \exp(-16844/RT)[\text{s}^{-1}]$ calculated by Simmie [6]. Based on similarity, the rate constant of the addition to O₂ is taken from that of acetyl radical (CH₃•CO) as calculated by Lee et al. [7]. As reported in Table 1, the fast decomposition of the α -radical dominates over the addition to oxygen for T≥500K. The branching ratio of Table 1 is calculated assuming O₂ concentration equal to that of a stoichiometric oxidation of 0.15% fuel in nitrogen, at 10 atm pressure, to be consistent with the experimental data of Veloo et al. [4, 5]. Based on this assumption, the low temperature oxidation of C₂-C₄ aldehydes (R_nCHO) is mainly related to the low temperature branching path of the corresponding R_n alkyl radicals.

Table 1. Relative selectivities of carbonyl radicals R_n•C=O addition (add.) to O₂ or decomposition (dec.) to CO and R_n alkyl radical.

	$R_n \cdot C=O$	
	[7]	[6]
$T [K]$	add.	dec.
450	0.68	0.32
500	0.22	0.78
600	0.01	0.99
700	0.00	1.00
800	0.00	1.00
900	0.00	1.00
1000	0.00	1.00

Results and discussion

The validation of the low temperature mechanism for propanal and *n*-butanal has been carried out by comparison with recently published species measurements in isothermal Jet Stirred Reactors by Veloo et al. at T=500-1100 K, p=10 atm and $\Phi=0.3, 0.5, 1.0$ and 2.0. Due to space limitation only the $\Phi=0.5$ cases are reported in Figure 2 and Figure 3 for propanal and *n*-butanal respectively. With regards to propanal oxidation (Figure 2), despite the overestimation (~40%) of hydrogen and formaldehyde formation at T=800-1000 K, the present model is able to correctly predict the main intermediate and product species both at low and intermediate temperatures.

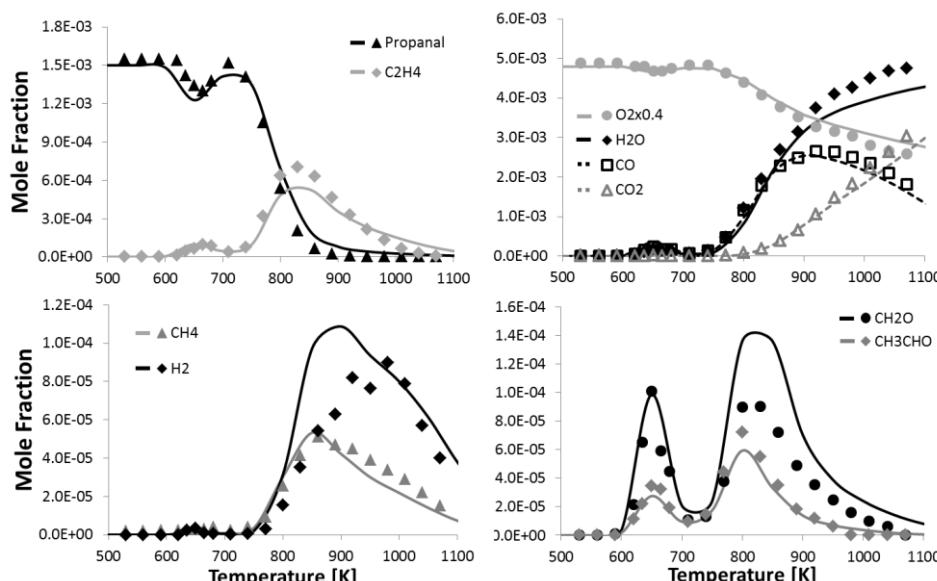


Figure 2. Experimental [4] (symbols) and calculated (lines) mole fraction profiles obtained from the oxidation of propanal (0.15%) in a JSR at $\Phi = 0.5$, $p = 10$ atm, and $\tau = 0.7$ s.

Concerning *n*-butanal oxidation (Figure 3), the mechanism correctly capture the onset of the low temperature reactivity, underestimating of ~20% the conversion in the Negative Temperature Coefficient (NTC) region. The lack of reactivity compared to the experimental measurements, results in an underestimation of propylene formation. In fact, propylene formation is mainly related to propyl radical low temperature reactions such as $n\text{-C}_3\text{H}_7+\text{O}_2 \Rightarrow \text{C}_3\text{H}_6+\text{HO}_2$ and hydroperoxy-propyl radical decomposition ($n\text{-C}_3\text{-QOOH} \Rightarrow \text{C}_3\text{H}_6+\text{HO}_2$). Considering that the data from Veloo et al. [4,5] constitutes the only experimental measurements at low temperatures for C₃-C₄ aldehydes in the literature, and that propane low temperature mechanism was recently revised and validated [8], no improvement margins exist at present. In fact a wider set of experimental conditions (i.e. ignition delay times at low temperatures) would be necessary to better assess model reliability.

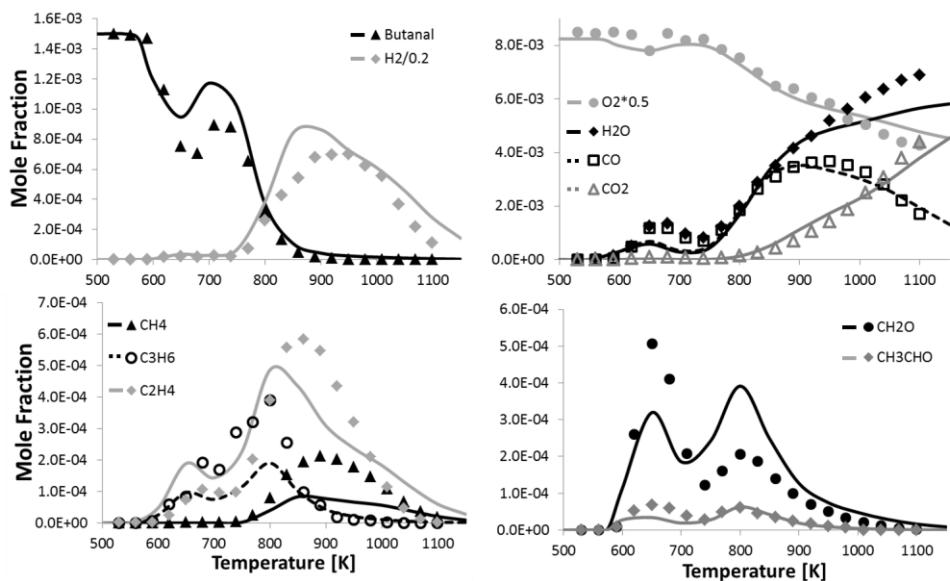


Figure 3. Experimental [5] (symbols) and calculated (lines) mole fraction profiles obtained from the oxidation of *n*-butanal (0.15%) in a JSR at $\Phi=0.5$, $p=10$ atm, and $\tau=0.7$ s.

Figure 4 compares propanal and *n*-butanal mole fractions profiles at the same experimental conditions. Figure 4 also reports, together with the measured values, the fuel profiles calculated with both POLIMI (solid lines) and Veloo et al. mechanism [4,5] (dashed lines). Both the mechanisms predict the low temperature reactivity increasing as *n*-butanal>propanal. This is justified by the fact that the propyl radical has a higher low temperature reactivity compared to the ethyl radical. According to POLIMI mechanism both aldehydes show the maximum low

temperature reactivity at ~ 650 K, while experimentally the relative minimum for *n*-butanal seems to be slightly shifted towards higher temperatures.

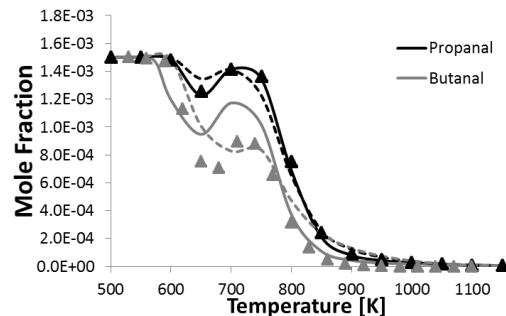


Figure 4. Comparison of propanal (black) and *n*-butanal (grey) mole fraction profiles. Experiments [4,5] (symbols), POLIMI mechanism (solid lines), Veloo et al. mechanism [4,5] (dashed lines) at $\Phi=0.5$, $p=10$ atm, and $\tau=0.7$ s.

A sensitivity analysis of OH formation has been carried out for *n*-butanal at 650 K. Results are reported in Figure 5. As expected the most sensitive reactions are those involving the low temperature branching path of *n*-propyl radical, with low temperature species such as *n*-propyl-peroxy radical ($n\text{C}_3\text{H}_7\text{OO}$), propyl-hydroperoxy radical ($n\text{C}_3\text{-QOOH}$) and peroxy-propyl-hydroperoxy radical ($n\text{C}_3\text{-OOQOOH}$).

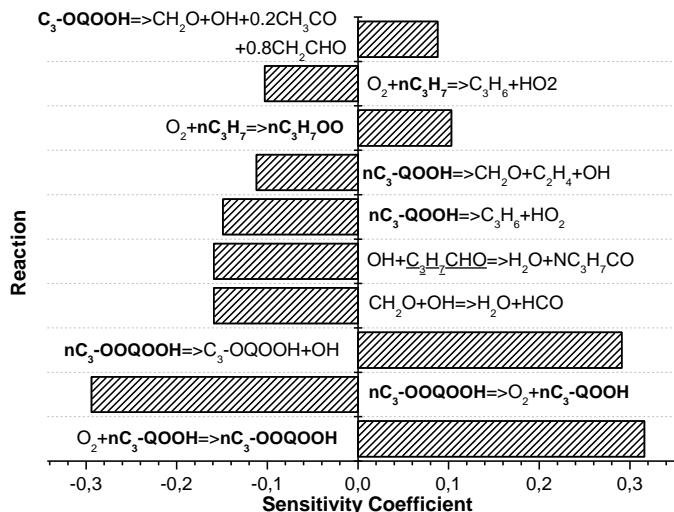


Figure 5. Sensitivity analysis of OH formation to rate constants for *n*-butanal oxidation at $T=650\text{K}$.

Conclusions

A detailed mechanism to describe the low temperature oxidation of propanal and *n*-

butanal was developed based on the low temperature oxidation of acetaldehyde and on the high temperature mechanism for C₃-C₅ aldehydes [3]. Aldehydes oxidation mainly proceed via hydrogen abstraction from the weakly bound aldehydic R_nH-C=O site forming the α -carbonyl radical R_n \cdot C=O. The decomposition of the α -radical to CO and the corresponding R_n alkyl radical is very fast, preventing any addition to O₂. Based on this assumptions, it is reasonable to assume that the low temperature oxidation of heavier aldehydes (R_nCHO) is mainly related to the low temperature branching path of the R_n alkyl radicals. Despite a quite satisfactory comparison with speciation measurements in Jet Stirred Reactor [4,5] the scarcity of experimental data on aldehydes low temperature oxidation prevents any wide range validations of the present mechanism. Due to the lack of symmetry introduced by the presence of the carbonyl moiety, the development of the detailed mechanism required the introduction of a large number of species in the global POLIMI mechanism (creckmodeling.chem.polimi.it). Reduction of the number of species through lumping will follow in a future study.

References

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