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Zeynep Serinyel, Guillaume Dayma, Philippe Dagaut. A detailed high-pressure oxidation study of n-pentanal. Proceedings of the Combustion Institute, 2024, 40 (1-4), pp.105254. 10.1016/j.proci.2024.105254 . hal-04654825

HAL Id: hal-04654825

<https://cnrs.hal.science/hal-04654825v1>

Submitted on 5 Sep 2024

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A detailed high-pressure oxidation study of n-pentanal

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Abstract

Oxidation of n-pentanal is studied in a jet-stirred reactor at 10 atm for four dilute mixtures with equivalence ratios 0.3, 0.5, 1 and 2 and between 500–1150 K. A detailed kinetic sub-mechanism is developed and used along with the mechanisms representing the oxidation of two branched isomers of pentanal, namely 2- and 3-methylbutanal. At all conditions, n-pentanal showed a strong low-temperature reactivity and an NTC region. Among the experimentally observed species, ones related to the low-temperature oxidation of n-butyl radicals can be found, consolidating the importance of the (n-1) alkyl radicals in aldehyde chemistry. The kinetic mechanism showed good agreement against the data as well as other speciation data at atmospheric pressure from literature. The present data are also compared to previous similar studies on the oxidation of C₃–C₅ aldehydes in the same JSR and where n-pentanal shows the highest global reactivity.

Keywords: pentanal; jet-stirred reactor; oxidation; chemical kinetics

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1. Introduction

Aldehydes are very important intermediates in alcohol oxidation. Recent research on the oxidation of higher alcohols showed the presence of aldehydes with the same carbon number such as n-butanol, n-pentanol, 2-methyl-1-butanol and iso-pentanol, all considered potential biofuels [1-5]. Moreover, aldehydes can easily form alkyl radicals (with 1 carbon atom less) due to the weaker acyl C-H bond, which is followed by the α -scission of the fuel radical. For higher aldehydes, this implies an important low-temperature reactivity involving the contribution of these alkyl radicals. Oxidation chemistry of the aldehydes is hence not only driven by its primary radicals but also by the fate of alkyl radicals.

Previous research on the oxidative speciation of higher aldehydes includes some detailed oxidation studied as in [6-8]. The study by Pelucchi et al [6] reports speciation data for the oxidation of normal C₄, C₅ and C₆ aldehydes at atmospheric pressure. Some of the authors also reported high temperature shock tube data on C₃-C₅ aldehydes [9]. In their speciation study, while all aldehydes showed low-temperature reactivity and a well-marked NTC region, n-hexanal appeared to be clearly more reactive than n-pentanal and n-butanal in the whole operating range. Previously, we have studied two branched C₅ aldehydes in a jet-stirred reactor at 10 atm and observed clearly different reactivities between 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB) with a very different specific pool of intermediate species [8]. The present study concerns the oxidation of the normal isomer of C₅ aldehydes, n-pentanal. It is performed under the same experimental conditions as its branched isomers, and the kinetic mechanism developed then, includes now the sub-mechanism of n-pentanal.

2. Experimental set-up (jet-stirred reactor) and kinetic mechanism

2.1 Experimental

Experiments were carried out in a fused silica jet-stirred reactor settled inside a stainless-steel pressure resistant jacket, the principles of which are described in detail in [10]. In summary, the reactor is a 4 cm diameter fused silica sphere equipped with 4 nozzles (1 mm i.d.) and has a volume of 42 cm³. The mixtures are highly diluted (0.1% fuel) in N₂ in order to avoid significant heat release and temperature gradients. An HPLC pump with an online degasser was used to deliver the fuel to an in-house atomizer-vaporizer assembly maintained at 200°C. The reactants were brought separately to the reactor to avoid premature reactions. After mixing at the entrance of the reactor, the reactants mixture was injected by 4 injectors providing stirring. Good thermal homogeneity along

the vertical axis of the reactor (gradients of ca. 1 K/cm) was observed during the experiments by thermocouple measurements (0.1 mm Pt-Pt/Rh-10%, located inside a thin-wall fused silica tube). The reacting mixtures were sampled using a movable fused silica low-pressure sonic probe. Analyses were performed online using a FTIR spectrometer (10 m path length, resolution of 0.5 cm⁻¹, and 200 mbar in the optical cell) and off-line by gas chromatography after collection and storage in 1 L Pyrex bulbs. The experiments were performed at 10.0 ± 0.1 atm, over the temperature range (530–1190) ± 4 K, and at a fixed mean residence time of 0.7 ± 0.03 s. The residence time was held constant by adjusting the gaseous flow rates at each temperature.

The uncertainty on the mole fractions is a result of the factors stated above as well as quantification being done using the effective carbon method [11] when a pure sample was not available. The overall uncertainty on the mole fractions is estimated to be within 15%.

2.2 Kinetic mechanism

The kinetic mechanism is based on that describing 2-MB and 3-MB oxidation with some modifications done in the C₀-C₂ subset, over the years. A sub-mechanism for n-pentanal oxidation is developed using similar rate rules for similar reactions and is included within the existing reaction mechanism. The rate constants estimated for various types of reactions are consistent with what was used in 2-MB and 3-MB oxidation, previously [8]. The present mechanism and the thermochemistry are provided as Supplementary Material with the references of all reactions therein. A particular attention was given to the low temperature sub-mechanism of the n-butyl radical. As recently shown by Keçeli et al. [12], the choice of thermochemical parameters may have a huge influence on the prediction of n-butane mole fraction profiles (or any fuel, as one may expect). For the RO₂/QOOH radicals, we have used the thermochemistry computed in [12] when available. Otherwise, these parameters were estimated based on group additivity [13]. The JSR simulations were carried out with the Perfectly Stirred Reactor (PSR) code of Chemkin II package [14].

3. Results and discussion

3.1 Experimental results and model comparison

Figure 1 shows experimental and simulated n-pentanal mole fraction profiles as a function of the reactor temperature for all the conditions selected in the present work. It is obvious from this figure that at any equivalence ratio there is a strong reactivity at low temperatures (~550–750 K) with also a pronounced NTC region (~650–750 K) for stoichiometric and rich

mixtures while reactivity appears to be sustained for lean mixtures. The mechanism predicts these tendencies very well.

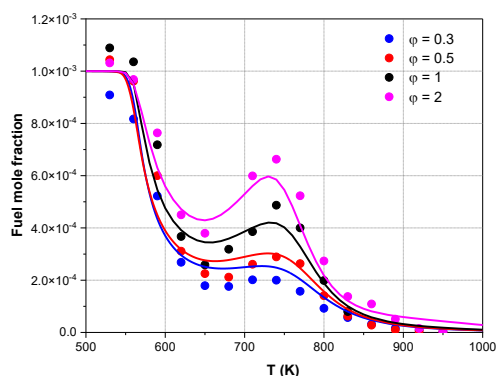


Figure 1. Mole fraction profiles of n-pentanal at all equivalence ratios, $p = 10$ atm, $\tau = 0.7$ s (symbols: data, lines: simulations).

Figures 2–5 show mole fractions of the intermediates and reaction final products as well as the fuel at all equivalence ratios. Among oxygenated

reaction intermediates, formaldehyde and acetaldehyde are the most abundant ones. Methacrolein is quantified with a maximum mole fraction of around 15 ppm, as well as some acetone in trace amounts. Cyclic ethers specific to n-butyl chemistry with a molecular formula of C_4H_8O were identified but only tetrahydrofuran showed a clear peak and hence is the only one quantified. It is solely formed from the 4-hydroperoxybut-1-yl radical, which requires a 7-membered ring intermediate of the n-butylperoxy radical prior to its formation and hence is not a major intermediate in this case. It is quantified with a maximum mole fraction of 20-25 ppm. Other cyclic ethers with 4 four carbon atoms were also identified, however, co-eluted, therefore their mole fractions could not be determined accurately.

It can be seen from these figures that model–experiment comparison is generally quite good. A small discrepancy can be observed in the prediction of the slight NTC behavior when $\phi = 0.3$ (Fig. 2), reflected in CO and H_2O profiles also. This discrepancy disappears for other mixtures.

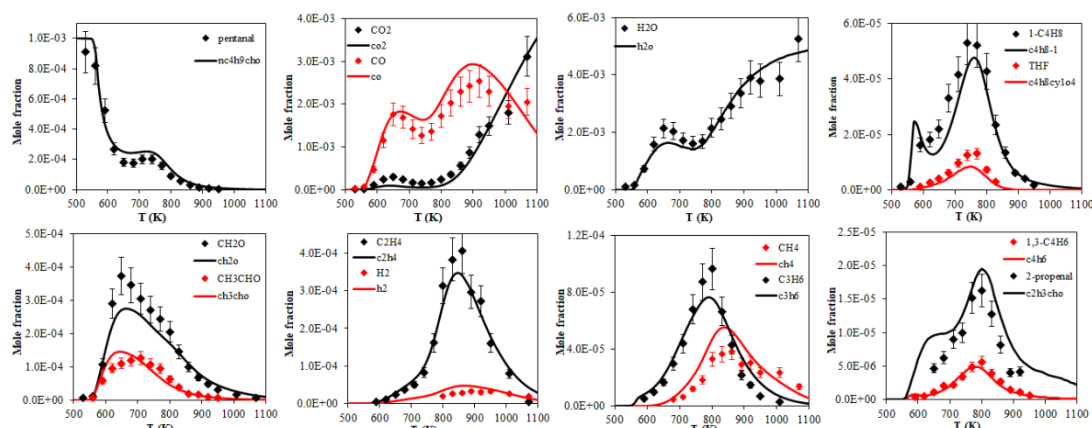


Figure 2. Mole fraction profiles for the $\phi = 0.3$ mixture, $p = 10$ atm, $X_{0,\text{fuel}} = 0.1\%$, $\tau = 0.7$ s (symbols: data, lines: simulations)

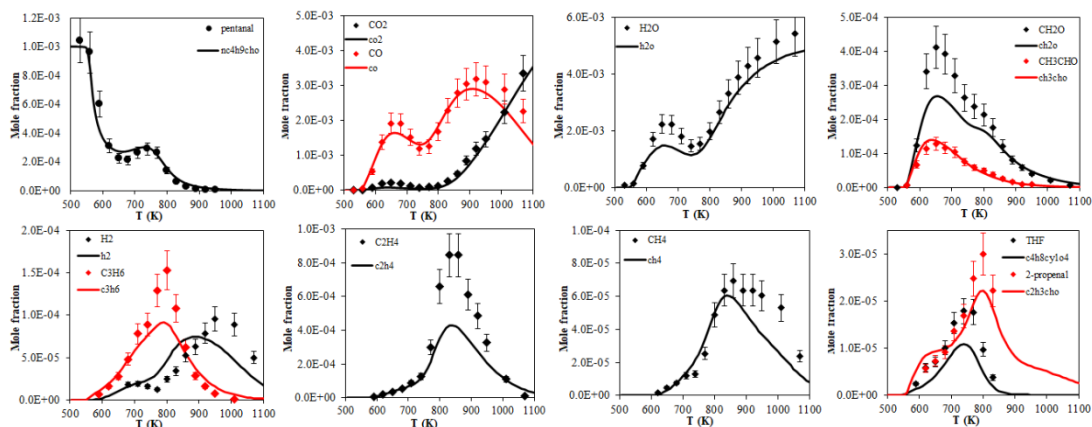


Figure 3. Mole fraction profiles for the $\phi = 0.5$ mixture, $p = 10$ atm, $X_{0,\text{fuel}} = 0.1\%$, $\tau = 0.7$ s (symbols: data, lines: simulations)

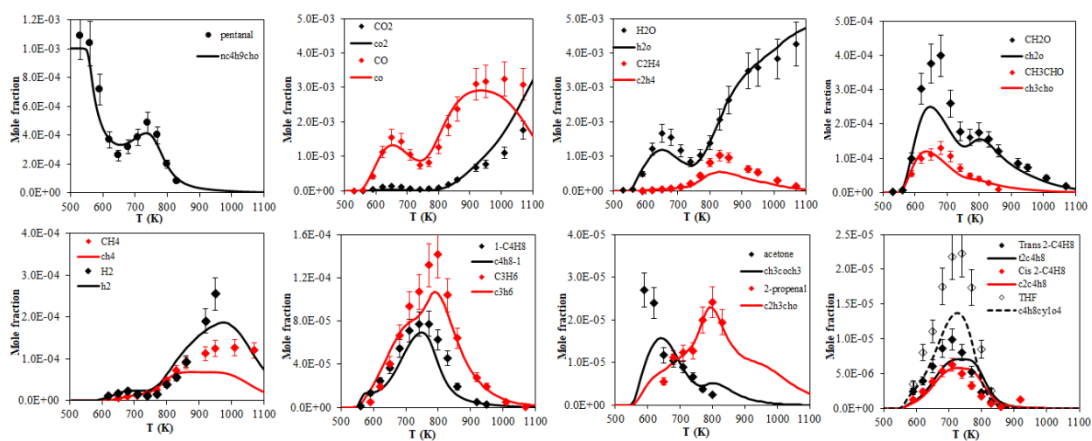


Figure 4. Mole fraction profiles for the $\phi = 1$ mixture, $p = 10$ atm, $X_{0,\text{fuel}} = 0.1\%$, $\tau = 0.7$ s (symbols: data, lines: simulations)

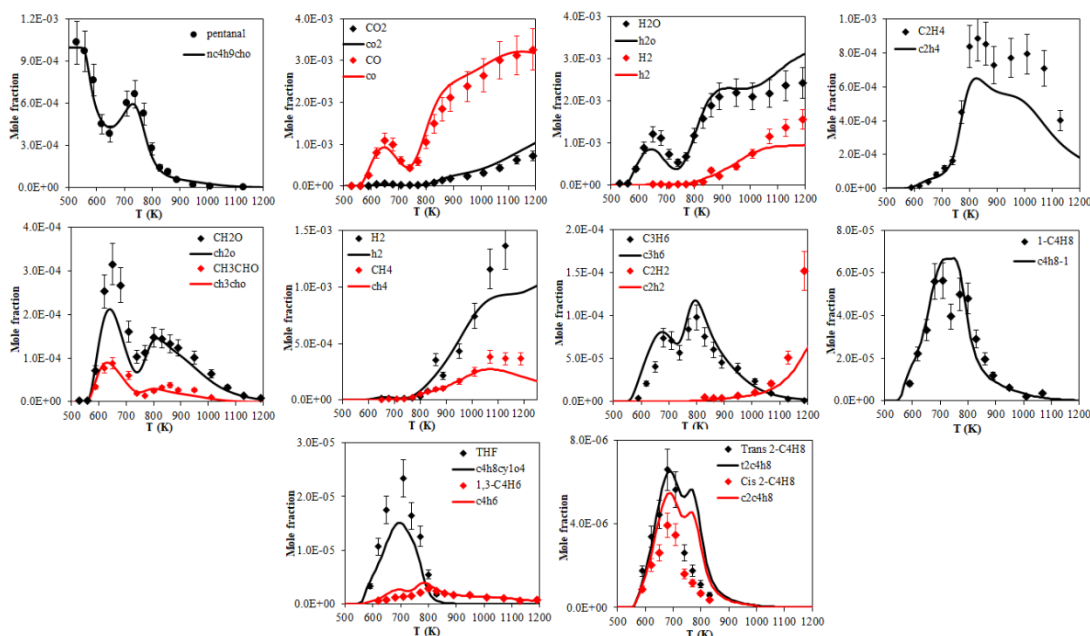


Figure 5. Mole fraction profiles for the $\phi = 2$ mixture, $p = 10$ atm, $X_{0,\text{fuel}} = 0.1\%$, $\tau = 0.7$ s (symbols: data, lines: simulations)

3.2 Reaction pathway analysis

A reaction pathway analysis showing the initial decomposition routes is given in Fig. 6. It is presented for the stoichiometric mixture at 600 K where the reactivity is just below its maximum. At this condition the fuel is mainly consumed by OH radicals (and HO₂ radicals to a lesser extent) forming five possible primary radicals. As expected, the acyl radical (n-C₄H₉CHO) formation is favored at any temperature. Almost half of the reaction flux forms this radical, which then decomposes via α -scission forming an n-butyl radical and CO. At any condition and/or temperature this is the preferred reaction pathway for this radical. This implies that the fate of n-butyl radicals is expected to have an important effect in n-pentanal oxidation. A similar role has been observed for sec-butyl and iso-butyl radicals in 2-methylbutanal and 3-methylbutanal oxidation, respectively [8]. n-Butyl radicals follow a classical low-temperature oxidation pathway by adding to molecular oxygen to form the n-butylperoxy radical ($\text{n-C}_4\text{H}_9 + \text{O}_2 \rightleftharpoons \text{C}_4\text{H}_9\text{O}_2$). Among the main reactions presented, the $\text{RO}_2 \rightleftharpoons \text{QOOH}$ type of isomerization reaction corresponds to 63% of the flux consuming this radical. For the isomerization, 7-membered ring transition state is less favored with 7% of the flux. However, this is the only pathway forming tetrahydrofuran (in small quantities). The more favorable isomerization pathway leads to the C₄H₈IOOH3j radical, which further follows a classical chain branching pathway finally forming acetaldehyde (40% of its formation) and $\bullet\text{CH}_2\text{CHO}$ (61% of its formation). This corresponds to 65% of the overall fate for this C₄ aldehydperoxide. Part of it can yield carboxylic acids along with acetone and acetaldehyde via the Korcek mechanism [15]. This is

one of the two pathways forming acetone, which is experimentally observed and quantified. However, no acids were identified experimentally. 24% of the n-butylperoxy radical forms n-butylhydroperoxide (C₄H₉IO₂H) by reaction with HO₂. All of the C₄H₉IO₂H yields n-butoxy radicals by O–O scission, then 100% of the n-butoxy radicals give n-propyl radicals and formaldehyde ($\text{n-C}_4\text{H}_9\text{O} \rightleftharpoons \text{n-C}_3\text{H}_7 + \text{CH}_2\text{O}$). Formaldehyde owes 27% of its formation to this reaction, while 95% of the n-propyl radicals are produced this way. At the temperature of analysis (600 K), n-propyl radicals completely add to O₂ forming n-propylperoxy radicals, which can then follow several reaction pathways. Its reaction with HO₂ ($\text{n-C}_3\text{H}_7\text{O}_2 + \text{HO}_2 \rightleftharpoons \text{n-C}_3\text{H}_7\text{O}_2\text{H} + \text{O}_2$) yields the n-propylhydroperoxide molecules, which accumulate at this temperature. CH₂O formation via n-C₃H₇O \bullet decomposition is hence rather unimportant among its other routes of formation. Note that formaldehyde peak is generally under-predicted while its prediction is good otherwise. For example, at its peak temperature (650 K) at any equivalence ratio, it is mainly (30–35%) formed by the reaction between HO₂ and $\bullet\text{CH}_2\text{CHO}$ radicals where the latter radicals are produced by the decomposition of the most abundant C₄ ketohydroperoxide (named as KHP in Fig 6). Therefore, any uncertainty related with the C₄ chemistry or the branching ratio of the reactions consuming this KHP affects the formaldehyde peak mole fraction.

The second abundant fuel radical is C₄H₈CHO-2, which completely adds to O₂ and mostly (79% of the QOOH flux) follows a typical low temperature chain branching pathway. Some of this QOOH decomposes via β -scission forming glyoxal and propene. Glyoxal accumulates at this temperature (20 ppm at 600 K and a maximum of 50 ppm at 750 K). However, it is not observed experimentally. It would be useful to point

out that not all intermediate species expected to be formed can be observed experimentally by our analytical means, and glyoxal is one of them (no response on FID). Therefore, it is difficult to comment on the accuracy the rate constant used for its

formation reaction. Also note that, there is very little propene at 600 K, which is formed by this reaction (20 ppm).

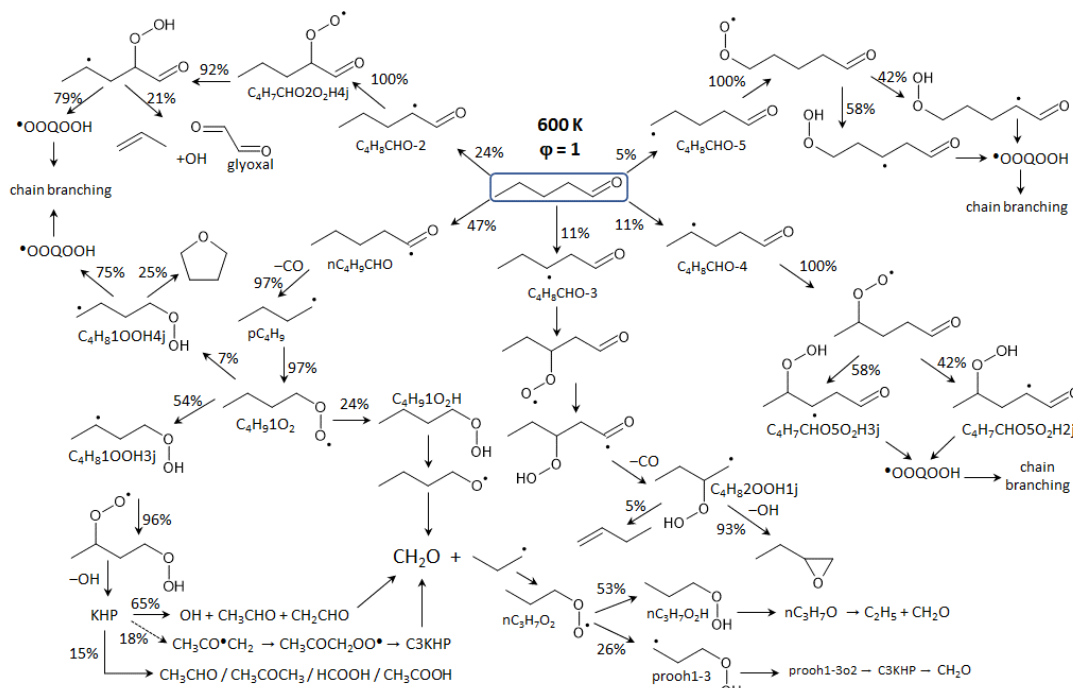


Figure 6. Reaction pathway analysis in n-pentanal oxidation, $T = 600$ K, $p = 10$ atm, $\phi = 1$, $X_{0,\text{fuel}} = 0.1\%$

The formation of the fuel radicals C_4H_8CHO-3 and C_4H_8CHO-4 correspond altogether to 22% of the fuel decomposition flux. They both follow typical low-temperature oxidation pathways. It can be noted that the most favorable QOOH formed in C_4H_8CHO-3 reaction pathway, is an acyl radical and hence loses a CO by α -scission rather than adding to O_2 . It thereby forms the $C_4H_8O_2$ radical, which is also typical of the sec-butyl radical chemistry. The fate of $C_4H_8O_2$ radicals is the propagation route forming of a C_4 cyclic ether (ethyloxirane) and OH radicals. Ethyloxirane is experimentally observed in a co-eluted peak of C_4H_8O , its formation results mostly from the QOOH radical, itself deriving from $nC_4H_9O_2$, however, not shown in this analysis done at 600 K as it corresponds to 2% of the flux. This cyclic ether reaches its peak mole fraction at ~ 700 K.

Although not shown here for the sake of clarity, a similar analysis was done at high temperature as well. Hydrocarbon species do not reach their peak mole fractions at the same temperature. For example, CH_4 peaks around 1000 K and is mostly formed through the reaction $CH_3 + HO_2 \rightleftharpoons CH_4 + O_2$ followed by the recombination of $CH_3 + H$ and H-abstraction reactions by CH_3 radicals. Ethylene peak is observed between 800–850 K, its mole fractions are under-predicted when $\phi > 0.5$. This could be due the fact that experimentally ethylene is expected to be consumed less as initial O_2 content decreases and that the mechanism does not seem to follow this trend. Note that ethylene is consumed by OH radicals mainly at ϕ

$= 0.3$ (H-abstraction and addition) and by H addition giving ethyl radicals at $\phi = 2$. A sensitivity analysis was done but was inconclusive as the most sensitive reactions were common at all equivalence ratios.

Propene, on the other hand, peaks around 800 K at all equivalence ratios except $\phi = 2$ where it shows two peaks, one at ~ 680 K and another one at ~ 800 K. In fact, the formation of propene is closely linked to the low-temperature chemistry proper to n-pentanal (following C_4H_8CHO-2 radical). It is mainly formed via the same reaction that forms glyoxal. Given that the NTC behavior is strongly marked especially at $\phi = 2$, propene therefore shows a behavior coherent with the NTC. This can also be observed in the data of Pelucchi et al. [6] where the initial fuel mole fraction is 10 times more and the residence time is roughly twice compared to the present experiments (Figure.7).

The Figure 7 shows the experimental data from literature in comparison with the present mechanism. The model-experiment agreement is very good, and the reaction intermediates identified are very similar despite the different operating conditions. Ethylene maximum mole fraction is observed at ~ 850 K; 30% of its formation occurs via the β -scission of n-butyl radicals while half of its formation is linked to the C_2H_5 chemistry, either by oxidation of ethyl radicals, or by HO_2 elimination from ethylperoxy ($C_2H_5O_2$) radicals. Isomers of butene are also formed in n-pentanal oxidation. 1-Butene is a direct product of the β -scission of the primary fuel radical 3 via $C_4H_8CHO-3 \rightleftharpoons C_4H_8-1 + HCO$. 2-Butene, on the other hand, is

formed in trace amounts via the reaction of HO₂ and methyl allyl radicals, which themselves are formed by H-abstraction on 1-butene.

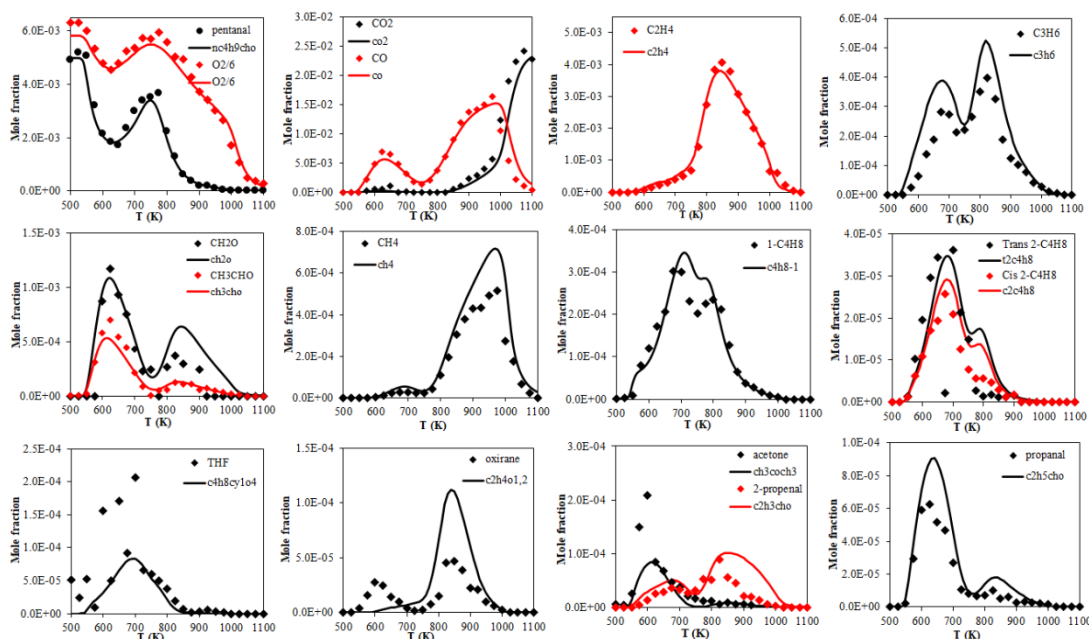


Figure 7. JSR data from literature [6] for n-pentanal oxidation and comparison with the present mechanism. Experimental conditions are: $P = 1$ atm, $\phi = 1$, $X_{0,\text{fuel}} = 0.5\%$, $\tau = 2$ s.

3.3 Comparison with smaller aldehydes and its isomers (2-MB and 3-MB)

Fuel conversion of different aldehydes C₃–C₅ are shown in Figure 8a. These include propanal, n- and iso-butanal previously oxidized in our JSR also at 10 atm and with a residence time of 0.7s [7, 16]. The initial mole fractions of propanal, and butanal isomers were 0.15%, as opposed to n-pentanal with 0.1%. It should be noted that a higher initial fuel mole fraction triggers reactivity such that a higher reactivity is to be expected at 0.15% than at 0.1%. However, this does not affect the discussion as the relative reactivities of these fuels are clearly very different. For example, iso-butanal shows a conversion close to zero at low temperatures, if its initial mole fraction were 0.1%, this would have been even less. In this sense, conversion profiles take this effect into account. The observation is that for normal aldehydes the chain length determines the reactivity of the fuel as well as the fact that the small low-temperature reactivity of propanal is sustained by the chain branching of its primary radicals rather than by the C₂H₅ radicals formed early during its oxidation (in analogy with n-butyl radicals in n-pentanal) which do not contribute to chain branching. One can also note that fuel conversion starts at higher temperatures compared to n-butanal and n-pentanal. Iso-butanal, on the other

hand, shows no conversion until high temperatures (> 750 K), probably because its most abundant radical eventually forms iso-propyl radicals that do not sustain low-temperature chain branching and also probably because its only primary radical that can lead to KHP formation through 6-membered ring transition states is the least abundant one. n-Pentanal, despite the fact that its initial mole fraction was less than that of the smaller aldehydes, shows the highest reactivity. Its longer chain allows it to produce 5 different primary radicals, which, given their linear structures, are able to maintain chain branching at low temperatures with more secondary carbon atoms than in ramified or shorter chains. Moreover, its acyl radical forms n-butyl radicals, as explained above, and contributing effectively to chain branching as well.

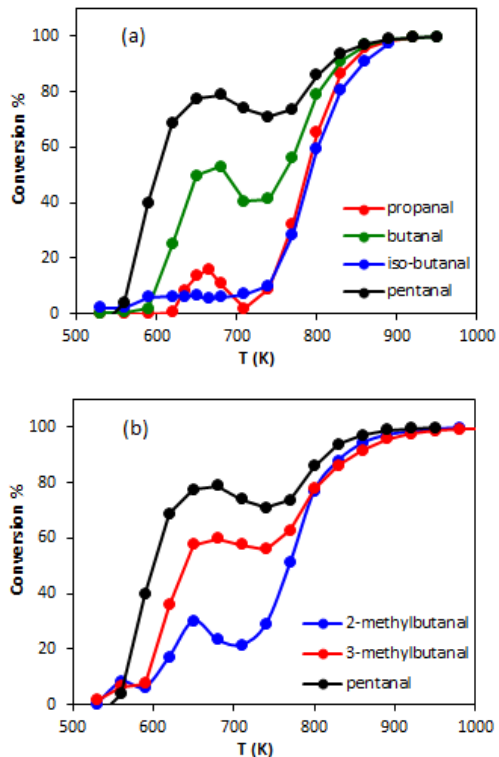


Figure 8. (a) Fuel conversion of propanal, n-butanal, iso-butanal and n-pentanal (b) Fuel conversion of n-pentanal, 2-methylbutanal and 3-methylbutanal. For both figures: $\phi = 0.5$, $p = 10$ atm, $\tau = 0.7$ s. Lines represent trends. 2-MB and 3-MB data from [8], propanal data from [16], n- and iso-butanal data from [7].

The Figure 8b illustrates the fuel conversion of three pentanal isomers under the same conditions, when $\phi = 0.5$, at 10 atm and 0.7 s of residence time. 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB) were previously investigated by our team [8]. Here the initial mole fractions are also the same (0.1%). Other equivalence ratios are not shown because the conclusion is the same. It is clear from this figure that among these C_5 aldehydes, the least reactive one is 2-MB and the most reactive one is n-pentanal, at all temperatures. In fact, its reactivity begins at even lower temperatures compared to 2-MB and 3-MB, for example its conversion reaches 50% at 600 K while at the same temperature the conversion of the branched isomers is less than 10%. The linear structure of n-pentanal facilitates low-temperature chain branching due to its primary radicals, at lower temperatures. The reactivity at low temperatures is also sustained by the n-butylperoxy radical chemistry. This role is taken by sec-butyl and iso-butyl radicals in 2-MB and 3-MB oxidation, respectively, as shown and discussed in [8]. The methyl branching in 2-MB and 3-MB on the other hand, lead to a least effective chain branching

compared to n-pentanal. The transition from NTC region to high-temperature regime, on the hand, appears to happen at roughly the same temperature.

4. Concluding remarks

In line with our previous studies on detailed oxidation of aldehydes, in this paper we report the first high-pressure oxidation of n-pentanal in a JSR for highly diluted mixtures. This study shows considerable reactivity of n-pentanal at all temperatures with a slight NTC for the leanest mixture and a more pronounced one for the richest. In this study a somewhat smaller pool of intermediate is observed experimentally compared to 2-MB and 3-MB and the intermediate species identified are very similar to those reported in the literature at atmospheric pressure. The present aldehyde mechanism is first tested on our experimental results as well as the only speciation data available in the literature and was found to be in very good agreement. Other validation data include the high-temperature ignition delay times measured in a shock tube as well as the pyrolysis of 3% n-pentanal [9] and are given in SM. For a better assessment of the NTC at $\phi = 0.3$, a more concentrated and/or leaner mixture can be tested and more detailed studies can be done with analytical equipment of high resolution. Global reactivity data such as ignition delay times would also be useful at low/intermediate temperatures in order to properly understand aldehydes and thereby the low/intermediate temperature chemistry of alkyl radicals.

Supplementary material

The kinetic mechanism, thermochemistry file and the experimental data are provided. Simulations of the n-pentanal data in [9] with the present mechanism are also provided in SM.

Acknowledgements

The authors acknowledge the support of Labex Caprysses (convention ANR-11-LABX-0006-01).

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