



An experimental and kinetic modeling study of the pyrolysis and oxidation of n -C₃–C₅ aldehydes in shock tubes



Matteo Pelucchi^{a,*}, Kieran P. Somers^b, Kenji Yasunaga^c, Ultan Burke^b, Alessio Frassoldati^a, Eliseo Ranzi^a, Henry J. Curran^b, Tiziano Faravelli^a

^a Dipartimento di Chimica, Materiali ed Ingegneria Chimica “G. Natta” Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

^b Combustion Chemistry Centre, National University of Ireland, Galway, University Road, Galway, Ireland

^c Department of Applied Chemistry, National Defense Academy, Hashirimizu 1-10-20, Yokosuka 239-8686, Japan

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ABSTRACT

Due to the increasing interest in the use of biofuels for energy production, it is of great importance to better understand the combustion and thermal decomposition characteristics of species such as aldehydes. These are known to be key intermediate products of transport fossil and bio-fuels combustion and are also dangerous pollutants emitted from combustion in internal combustion engines and from gasification of biomasses. In this study, an experimental and kinetic modeling investigation of propanal, n -butanal and n -pentanal pyrolysis and oxidation in two shock tube facilities was carried out. Experiments were performed in a single pulse shock tube to determine the speciation profiles of the fuels and intermediate species under pyrolysis conditions for mixture of pure propanal/ n -butanal/ n -pentanal (3%)–Ar (97%), at averaged reflected pressure of 1.9 atm and at reflected shock temperatures of 972–1372 K. Additionally, ignition delay times for mixtures of pure propanal/ n -butanal/ n -pentanal (1%)–O₂/Ar were measured in the temperature range 1136–1847 K, at pressures of 1 and 3 atm, and at equivalence ratios of 0.5, 1.0 and 2.0.

A comprehensive sub-mechanism for the high temperature kinetics of the three aldehydes was developed. This scheme was then coupled with NUIG (National University of Ireland, Galway) and POLIMI (Politecnico di Milano) C₀–C₄ kinetic schemes. The inclusion of the aldehydes sub-mechanism in two different kinetic environments, required modifications for the H-abstraction reactions, due to different rate rules in use in the two kinetic environments, and due to differences in the C₀–C₄ kinetic schemes. Both of the models were validated and showed good agreement with the new experimental data. The mechanisms are also satisfactorily compared with ignition delay times, speciation profiles and laminar burning velocities previously published in literature. Reaction pathways and sensitivity analyses were also performed to highlight the important reaction steps involved in the pyrolysis and oxidation processes. The major differences between the models and the experiments have to be attributed to the chemistry of the smaller species, more than to aldehyde specific reactions. This work further highlights the relevant role of the C₀–C₄ sub-mechanism, mainly in terms of a unification process that needs to start from the smaller species chemistry in order to obtain an unambiguous description of any fuel investigated.

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1. Introduction

The depletion of fossil fuel reserves and the stringent targets for air pollution reduction have largely increased the focus on gaseous, liquid and solid biofuels as a sustainable source of energy for transport, domestic and industrial applications. Biomasses can be used to produce either liquid or gaseous biofuels for transportation

purposes (hydrogen, methane, ethanol and long chain alcohol, dimethyl ether, diesel) through different processes such as Biomass-To-Liquid (BTL) or as a side product of Gas-To-Liquid (GTL) processes in Fischer–Tropsch synthesis. Similarly, municipal solid waste (MSW), agricultural and forest residues can also be converted to feedstock for energy production through gasification or combustion, followed by conventional power generation cycles.

Within this scenario, low and high molecular weight aldehydes are known to be toxic, some of them carcinogenic, and precursors of free radicals leading to the formation of ozone and urban smog

* Corresponding author.

E-mail address: matteo.pelucchi@polimi.it (M. Pelucchi).

[1]. C₄ and C₅ aldehydes belong to the class of non-regulated pollutants and they are classified as mobile source air toxic (MSAT) compounds. Recent fundamental studies of biofuel combustion have addressed the strong belief that long-chain alcohols (propanol, butanol, pentanol and related isomers) are likely to be used as an alternative to conventional gasoline (*n*-butanol and *iso*-pentanol mainly) either as additives in order to reduce pollution in terms of PAH, particulates and soot formation. Fundamental studies on the oxidation of alcohols identified the presence of aldehydes as intermediate products derived from radical as well as molecular dehydrogenation reactions [2–15].

Aldehydes are products of partial or incomplete combustion and they are released into the atmosphere from conventional spark ignition (SI) gasoline and compression ignition (CI) diesel engines, and also from biomass gasification or aerobic treatments [16]. Grosjean et al. [17] studied carbonyl emissions from light-duty and heavy-duty vehicles on a motorway tunnel, detecting emissions of saturated, unsaturated and aromatic aldehydes. Zervas [18] analyzed the exhaust gases from a diesel engine recording high emission of carbonyl compounds, particularly when synthetic fuels were tested compared to a commercial fuel. Karavalakis et al. [19] highlighted how the use of a Euro4 diesel engine increases the emissions (aldehydes and ketones) compared to a Euro3 engine identifying linear aldehydes from formaldehyde up to C₅–C₆ and aromatic aldehydes. De Abrantes and co-workers focused on formaldehyde and acetaldehyde emissions from diesel engines [20], highlighting higher concentrations than those observed in spark ignition engines. Gasoline and diesel engine emissions of aldehydes were also compared by Roy [21] through high performance liquid chromatography. Significant and comparable amounts of formaldehyde, acetaldehyde and propanal were detected from SI and CI engines investigating different injection technologies. Schauer [22] measured the emissions of aldehydes from a gasoline-powered vehicle, detecting concentrations in the order of those measured for diesel engines. Other works in recent years focused on the influence of diesel–biodiesel blended fuels on carbonyl emissions, agreeing that alternative fuel blending increases the release of aldehydes and that the engine technology influences the phenomena as much as the kind of fuel blend itself [23–27].

From a pure chemical kinetics perspective aldehydes are primary stable intermediate products of biofuel oxidation and pyrolysis, influencing reaction pathways and important combustion properties [28]. Therefore their combustion behavior is non-negligible with respect to designing more efficient and environmentally friendly combustion systems. For all of these reasons, the understanding of combustion kinetics of aldehydes and furthermore a deeper understanding of the reactivity of the carbonyl side of the molecule (R–CH=O) under combustion or pyrolytic conditions, play a crucial role in the capability of kinetic mechanisms to better predict pollutant release from both conventional and renewable fuels.

Since the pioneering work of Dean and co-workers [29] and of Hochgreb and Dryer [30], several kinetic studies on the pyrolysis and oxidation of formaldehyde at low- and high-temperature were undertaken [31–38].

Similarly, acetaldehyde oxidation has been described in detail by different authors. Dating back to the early 1970s Halstead et al. [39] discussed cool flames phenomena and low-temperature oxidation. Oscillatory ignitions in the low-temperature regime were studied in the early 1980s by Gray and co-workers [40], and in the 1990s by Cavanagh et al. [41] and by Di Maio et al. [42]. Kaiser et al. proposed a model to describe the negative temperature coefficient (NTC) behavior of acetaldehyde [43]. The high-temperature oxidation of acetaldehyde was investigated by Dagaut et al. [44] in a jet-stirred reactor and in a shock tube, while Hidaka and co-workers studied its pyrolysis in a single-pulse shock

tube [45], and Yasunaga et al. [46] suggested a mechanism describing the oxidation and pyrolysis for the high-temperature regime.

Da Silva and Bozzelli [47] calculated the enthalpies of formation of C₂ to C₇ *n*-aldehydes through quantum chemical calculations and determined bond dissociation energies (BDE) for all C–C and C–H bonds in the molecules. Their study revealed that the R–CH₂CH=O bond is the weakest bond in all the aldehydes larger than acetaldehyde, due to the formation of the resonantly stabilized vinyloxy radical. Kaiser [48] developed a chemical kinetic model to describe propanal oxidation in the temperature range 400–700 K. An experimental and modeling study at higher temperatures was carried out by Lifshitz and co-workers [49]. They investigated the thermal decomposition of propanal in a single pulse shock-tube under pyrolysis conditions. A sub-mechanism of 52 elementary reaction steps and 22 species was developed, and the kinetic analysis emphasized the importance of unimolecular initiation reactions involving a C–C bond breaking in predicting the intermediate and product species. Furthermore, the species profile predictions were found to be sensitive to the ratio between abstraction by ethyl radical on the fuel molecule and ethyl radical decomposition to form ethylene and a hydrogen atom. Kasper et al. [50] studied the combustion chemistry of propanal in a stoichiometric flame at low pressures with molecular beam mass spectrometry, highlighting, under the investigated conditions, the importance of alkyl radical addition to the fuel molecule and the need of more detailed kinetic studies to assess the relative importance of available reaction pathways. Akih-Kumgeh and Bergthorson [51] studied the ignition of propanal in a shock tube and developed a mechanism underlining the importance of the initiation reaction forming \dot{C}_2H_5 and HCO and the H-atom abstraction reactions from the alpha-carbonyl site in predicting ignition delay times. Laminar flame speeds were measured by Veloo et al. [52] together with jet-stirred reactor experiments to quantify reactant, intermediate and product concentrations. A model to describe the low- and high-temperature oxidation of propanal was then developed and validated.

Veloo and co-workers also studied *n*-butanal and *iso*-butanal oxidation in laminar flames and in a jet-stirred reactor proposing a comprehensive mechanism for low- and high-temperature combustion consisting of 244 species and 1198 elementary reaction steps [53]. The authors highlighted the importance of \dot{C}_3H_5 radical distribution and other key reaction subsets of the mechanism. An interesting comparison between *n*- and *iso*-butanal and propanal is also shown for flame speed data, with an emphasis on radical species profiles such as HCO and OH of high importance in flame propagation phenomena. Davidson and co-workers investigated the ignition behavior of *n*-butanal [54] as part of an update to the Dooley et al. methyl butanoate mechanism [55]. Zhang measured ignition delay times for *n*-butanal [56] and *i*-butanal [57] over a wide range of equivalence ratios, pressures and temperatures, and developed kinetic sub-models for both of the C₄ aldehydes based on a literature review and validated them against the measured data.

To the best of our knowledge, no experimental measurements currently exist for *n*-butanal pyrolysis and *n*-pentanal pyrolysis and oxidation. Furthermore, despite C₃–C₅ aldehydes being included in many hydrocarbon and bio-fuels kinetic models, no studies have specifically addressed to develop and validate an oxidation mechanism for *n*-pentanal. There have clearly been significant efforts focused on understanding the combustion behavior of aldehydes. Yet a consistent and detailed summary of their combustion behavior is still somewhat lacking in the literature.

Two important goals support and justify the present work. Firstly, it provides new experimental data on the pyrolysis and the auto-ignition behavior of C₃–C₅ aldehydes, in order to extend the database available for high-temperature combustion

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