An experimental and kinetic study of propanal oxidation

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ARTICLE INFO

ABSTRACT

Propanal is a critical stable intermediate derived from the oxidation of 1-propanol, a promising alcohol fuel additive. To deepen the knowledge and accurately describe propanal combustion characteristics, new burning velocity measurements at different temperatures were carried out and a new detailed kinetic mechanism for propanal was proposed. Experiments were performed using the heat flux method and compared with literature data. Important discrepancies were noted between the new and available data, and possible reasons were suggested. Flow rate sensitivity analysis highlighted that, as expected, the important reactions influencing the propanal oxidation in flames are pertinent to H_2 and CO submechanism. Current mechanism is based on the most recent Konnov model, extended to include propanal chemistry subset. Rate constant parameters were selected based on careful evaluation of experimental and theoretical data available in literature. Model validation included assessment against a large set of combustion experiments obtained at different regimes, i.e. flames, shock tubes, and well stirred reactor, as well as comparison with the semi-detailed (lumped) kinetic mechanism for hydrocarbon and oxygenated fuels from Politecnico di Milano, detailed kinetic model from Veloo et al. and low temperature oxidation of aldehydes kinetic model of Pelucchi et al. The proposed model reproduced experimental burning velocities, ignition delay times, flame structure and JSR data with an overall good fidelity, while it reproduces only qualitatively the species distribution of propanal pyrolysis.

1. Introduction

The use of short-chain aliphatic alcohols as transportation fuels may contribute to the abatement of harmful anthropogenic emission of air pollutants, such as CO and HC in spark ignition engines [1,2], as well as of soot formation and particulate matters in compressed ignition engines [3]. However, alcohol oxidation can lead to the formation of undesirable toxic carbonyl molecules, such as saturated and unsaturated aldehydes, which can appear in nonnegligible amounts in the exhaust gases of internal combustion engines. Their levels are extremely variable and hard to quantify, varying on alcohol fuel and engine types, loads, speeds, and operating conditions, therefore aldehydes have been the subject of dedicated studies [4–6].

With the purpose to understand the combustion chemistry and reactivity of such pollutants and reveal their formation mechanism, acquiring of new experimental data and the use of kinetic modeling is fundamental. While formaldehyde and acetaldehyde combustion chemistry has been extensively investigated in literature, the attention on propanal, C_2H_5CHO, oxidation kinetics is still insufficient and more fundamental studies are desirable.

Earlier studies on C_2H_5CHO oxidation and reactivity were mainly performed at relatively low temperatures in static vessels [7–14]. In Newitt et al. [7] study, reaction intermediates of propanal oxidation were analyzed in a static reactor at different conditions, at 508–633 K, from lower to upper slow-combustion zone. The formation of stable peroxide as initial product was found at all tested conditions. Salooja [8] using a flow reactor observed that the reactivity of $C_1–C_5$ aldehydes does not increase with increasing of molecular size. The author found C_2H_5CHO less reactive than CH_3CHO, denoted as the most reactive, but surprisingly C_2H_5CHO had shown a lower ignition temperature.

First numerical investigation of low temperature CH_3CHO and C_2H_5CHO oxidation was performed by Griffith et al. [9], on the basis of experimental data obtained in a coated Pyrex vessel; a successive account based on their observations was made by Bell et al. [10], investigating the effect on C2-C3 aldehydes oxidation caused by using two different reactors, i.e., nitric acid washed and potassium chloride coated vessels at 120–165°C. Under the tested conditions, the effect of the potassium chloride coating was to promote the onset of cool flame, observed at the low temperature of 393 K.

Baldwin et al. [11–12] evaluated rate constants of elementary reactions pertinent to a basic mechanism of C_2H_5CHO oxidation at low temperatures using an aged boric-acid coated vessel. Acetaldehyde formation in the C_2H_5CHO oxidation was found to be generated by a radical attack to the CH_2-group [11]. It was

also ascertained that the aldehydic C−H bond of formaldehyde was much stronger than in C_2H_5CHO [12]. An experimental study on the combustion chemistry of C_2H_5CHO by molecular beam mass spectrometry (MBMS) was carried out by Kaiser [13] in a static reactor at pressures of 50–120 Torr and temperature range of 553–713 K; a kinetic mechanism was also proposed [14].

A pressurized-driver single-pulse shock tube (SPST) was used by Lifshitz et al. [15] to study the thermal decomposition of C_2H_5CHO between 970 and 1300 K. A kinetic mechanism composed by 52 elementary reactions and 22 species was developed and validated against experiments. The authors highlighted the key role of the rate of dissociation of unstable free radicals for the products composition. Several modern experimental works were conducted in shock tubes as well [16,17,21,22]. Akih-Kumgeh and Bergthorson [16] investigated the effect of diverse oxygenated functional groups on hydrocarbons oxidation by measuring ignition delay times (IDTs). A C_2H_5CHO kinetic model was also suggested. Reaction pathway analysis has shown the important effect of H-abstraction in C_2H_5CHO consumption. A sub-mechanism for high temperature kinetics of $C_3−C_5$ n-aldehydes was presented by Pelucchi et al. [17] and combined with the $C_0−C_4$ kinetic mechanisms of NUIG [18] or Polimi [19] models. Assessments were performed against new shock tube experimental data and burning velocity data from literature [20]; an overall good agreement was found for both models. Authors attributed the major differences between the models and experiments to the different chemistry of the smaller species. Ignition delay times of propanal were measured by Yang et al. [21] in a shock tube in the temperature range of 1050–1800 K. A kinetic mechanism consisting of 250 species and 1479 reactions was proposed and validated against IDTs experimental data [21]. Koroglu and Vasu [22] investigated propanal pyrolysis and oxidation over the temperature ranges of 1192–1388 K and 1129-1696 K, respectively, and tested three different mechanisms, namely, Akih-Kumgeh and Bergthorson [16], modified NUIG and modified Polimi [17]. Based on sensitivity analysis, Polimi model was optimized and it showed an excellent agreement with IDTs experimental data [22].

Several flame studies are available in literature [20,23,26–29]. Burluka et al. [23] employed a spherical combustion chamber to measure the laminar burning velocity, S_L of C_3H_6O isomers (propylene oxide, propanal and acetone) at 298 K. Experimental data were compared with numerical simulation based on a modified version of the Konnov mechanism [24], which was extended to include chemistry of acetone and propylene oxide oxidation. It is important to highlight that the model contained a concise sub-mechanism for C_2H_5CHO combustion, where only the primary intermediate C_2H_5CO was considered. Results showed that the model had only qualitative agreement with the experimental data, under predicting the experimental data at all equivalence ratios, Φ, investigated. In an attempt to improve the model predictions, Burluka et al. [23] explored further possible break-up routes for propanal. Based on these investigations, authors suggested implementing C_2H_4CHO radical into the model to increase the modeled burning velocity at all Φ studied. Counterflow, twin-flame configuration was applied by Veloo et al. [20] to measure the laminar burning velocity of C_2H_5CHO at 343 K. Moreover, a jet-stirred reactor was employed to determine profiles of reactants, products and several stable intermediates, over the temperature range of 500–1100 K. Experimental results were subsequently used to validate the model of Dayma et al. [25], which was extended to consider specific reactions of C_2H_5CHO oxidation. IDTs data from [16] were also considered to validate the mechanism. Good agreement was found between numerical and experimental data. Gong et al. [26] measured the laminar burning velocity of C_2H_5CHO and other oxygenated fuels at atmospheric pressure in a cylindrical combustion bomb. The effect of the different functional groups on the fuel reactivity was analyzed.

Furthermore, an updated version of Aramco mech. 1.3 [18] was used to simulate their experiments and literature data from [20], obtaining a satisfactory and good consistencies, respectively.

MBMS was applied in the work of Kasper et al. [27] to determine the products of C_2H_5CHO oxidation in a stoichiometric low pressure flat flame. A considerable amount of oxygenated compounds with high molecular mass was detected in reaction intermediates. Vasu and coworkers [28] used multiplexed photoionization mass spectroscopy to investigate low temperature combustion of saturated and unsaturated aldehydes. Primary products for the propanal oxidation in the NTC region were found to be C_2H_4, CH_2O and CH_3CHO. Dias et al. [29] determined the flame structure of low pressure $C_2H_5CHO + H_2 + O_2 + Ar$ flames at stoichiometric and rich conditions through MBMS investigation. Authors observed that the small hydrocarbon content in the burnt gases was increasing as Φ increased; on the contrary, oxygenated molecules content was found following a reverse trend. An extended version of the UCL mechanism, modified to take into account the C_2H_5CHO kinetics was also proposed and a good agreement with experimental data was found.

In addition to the above mentioned kinetic works associated with experimental analysis [15–17,20,22,23,26,29], other studies were also performed. Ranzi et al. [19] developed a reaction scheme for hydrocarbon and oxygenated fuels using S_L data of Burluka et al. [23] to validate it for C_2H_5CHO oxidation. Modeling showed good agreement up to stoichiometric condition, but remarkable inconsistency was found for higher fuel concentrations. Kinetic model developed in [17] was successively modified by Pelucchi et al. [30] to examine low temperature oxidation of aldehydes. Good agreement was achieved when the model was compared with JSR data from [20].

Table 1 summarizes the most recent kinetic works on C_2H_5CHO decomposition, oxidation and combustion as well as the literature data used for their validation. It has to be highlighted that most of the proposed kinetic models have been tested only against one type of experiments.

The major goal of this study was to develop a new detailed kinetic mechanism of C_2H_5CHO oxidation. New burning velocity measurements, obtained with the heat flux method and therefore free from stretch effects, along with S_L literature data [20,23,26], performed with different methods, were used to assess the proposed model. The objective of this approach was to try to discern the nature of discrepancies that have arisen between experimental and modeled S_L came out in [23] and to check and compare the consistency of the different burning velocity measurements by using a different experimental method. Additionally, the new kinetic model was assessed with ignition delay times data from [16,21], propanal pyrolysis experiments from [15,17], jet stirred reactor data from [20], low-pressure flame structure [29], and, finally, compared with Veloo [20] and Polimi mechanism [19] predictions. Polimi semi-detailed (lumped) mechanism was tested in the current study since it is well established for high temperature combustion and pyrolysis of different fuels, and assessed against burning velocities of $C_0−C_4$ hydrocarbons and oxygenated fuels, including propanal experimental data from [23]. Polimi was also tested in several of our recent publications [31,32], and its modeling performance was found superior to the other kinetic mechanisms analyzed.

2. Experimental

In this work, the heat flux method has been used to determine the laminar burning velocity of C_2H_5CHO at $T = 298$, 323, 343, and 393 K, 1 atm and over the Φ range of 0.7–1.5 and compared with previous literature data obtained in spherical flames [23,26] and using counterflow technique [20]. Test fuel was provided by Alfa