Laminar burning velocity of acetic acid + air flames

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A B S T R A C T

Laminar burning velocities of acetic acid + air flames at 1 atm and initial gas temperatures of 338 K, 348 K, and 358 K were determined using the heat flux method. Measurements were performed in non-stretched flames, stabilized on a perforated plate burner at adiabatic conditions. Due to experimental problems related to the corrosiveness of acetic acid towards the burner material, the uncertainty of the burning velocities was relatively high up to ± 2 cm/s. Seventy reactions pertinent to acetic acid and ketene have been reviewed and detailed reaction mechanism for acetic acid combustion was developed. The model over-predicts measured burning velocities by about 3 cm/s. The mechanism was also tested comparing with flame structure of the low-pressure flame of acetic acid (Leplat and Vandooren, 2012). Good agreement with the concentration profiles of major products was found, however several minor intermediates were over- or under-predicted by the model. To elucidate reactions responsible for the differences observed, the sensitivity analysis was performed. It was found that the calculated burning velocities are insensitive to the reactions of acetic acid and mostly governed by C1 chemistry typical for all hydrocarbons and by reactions of ketene. Possible modifications of the rate constants within the evaluated uncertainty factors were discussed.

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1. Introduction

Carboxylic acids are abundant species in the environment that originate from both anthropogenic and biogenic sources. Their presence in soil, rain water and in the atmosphere has been well documented [1]. Acetic acid, CH_3CO_2H, is one of the most common carboxylic acids with high concentrations registered in urban areas. It is believed that the increased levels of acetic as well as other carboxylic acids are caused by traffic, a claim supported by many studies. For instance, Kawamura et al. [2] investigated emissions of gasoline engine and suggested motor exhaust to be the important source for organic acids including CH_3CO_2H. The same conclusion was reached by Talbot et al. [3], who studied direct emissions from vehicles and bio-mass burning. It was seen that both sources generated large quantities of CH_3CO_2H. The presence of carboxylic acids in the atmosphere in an urban area of São Paulo was measured by Souza et al. [4]. The results indicated that the acids showed both diurnal and nocturnal variations, with increased concentrations during night time. The authors suggested that this could be caused by photochemical reactions and/or emissions directly from fossil fuel combustion. Zervas et al.

investigated emissions of a spark ignition [5] and compression ignition [6] engines. Several fuels were investigated and the results indicated that the emissions of CH_3CO_2H were increased when the equivalence ratio was decreased. Addition of toluene was seen to enhance the emission of acetic acid [5]. Similar results were found in the study of the compression engine [6]. Although aldehydes were sometimes considered to be precursors of acids, it is noteworthy that Zervas et al. [6] measured a 6.5 times larger formation of organic acids than aldehydes.

In order to understand the formation of organic acids during combustion, Zervas [7] experimentally measured species profiles of burner stabilized propane, isooctane and toluene/isooctane flames using chromatography with a flame ionization detector. Maximum concentration of CH_3CO_2H was found at lean conditions in all flames. This is in agreement with the engines results [5,6]. A clear relation between the formation of C2 radicals and the production of CH_3CO_2H was observed, as C2 radical species are considered to be major precursors of CH_3CO_2H. To further investigate the formation mechanism of acetic and other acids, Battin-Leclerc et al. [8] developed a model and simulated the experimental results from the propane flames by Zervas [7]. While the mechanism was in acceptable agreement with these scarce experimental data, it failed at reproducing the increasing emissions of CH_3CO_2H experimentally observed at leaner conditions. The mechanism presumed that the formation of acetic acid is mainly driven by the CH_3CO + OH reaction.

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Further validation and improvement of the model developed by Battin-Leclerc et al. [8] was hampered by the lack of experimental studies of acetic acid combustion. Essentially, only two reports were available: on investigation of the flammability limits of acetic acid [9], and on its oxidation in a flow reactor [10]; a vast majority of kinetic studies outlined in the following was focused on CH_3CO_2H thermal decomposition or reactions at atmospheric conditions. Most recently, acetic acid flames stabilized at 50 mbar were investigated by Leplat and Vandooren [11]. Species profiles were obtained using molecular beam mass spectrometer and a kinetic model was created to simulate the experimental results. The detailed mechanism of Leplat and Vandooren was based on the ethanol mechanism developed by the same group [12]. Additional acetic acid reactions important for the combustion were added and the choice of their rate constants was outlined. While the mechanism was mainly constructed using the rate constants suggested in the literature, some modifications and assumption were made in order to improve the model behavior.

The chemistry of acetic acid is of importance in combustion of renewable oxygenated fuels, namely ethyl esters [13,14]. These esters may decompose directly forming CH_3CO_2H, and therefore Gasnot et al. [13] introduced several reaction of CH_3CO_2H + radicals assuming H atom abstraction from methyl group forming CH_2CO_2H only and assigning generic rate constants suggested by Warnatz [15] for reactions with primary H atoms of hydrocarbons. Leplat and Vandooren [11] introduced several reactions of CH_3CO_2H + radicals for H atom abstraction from acidic group forming CH_3CO_2 and assumed these rate constants similar to H atom abstraction from alcohol group. Ren et al. [14] constructed a model for C3–C5 ethyl esters decomposition and adopted several reactions of CH_3CO_2H + radicals from Leplat and Vandooren [11] without modification. Meanwhile theoretical studies of H atom abstraction reactions from acetic acid [16] and other relevant species have been published that can certainly help improving the acetic acid kinetic sub-mechanism.

The goal of the present study was therefore twofold: (a) to determine the laminar burning velocities, S_L, of premixed acetic acid + air flames at atmospheric pressure, and (b) to extend a recently updated detailed kinetic mechanism for small oxygenated fuels [17] by reactions of acetic acid and validate it. Moreover, the present mechanism was tested using experimental data from the low-pressure flames [11].

2. Experimental details

The heat flux method was used to determine the laminar burning velocities of premixed acetic acid + air flames at atmospheric pressure. The acetic acid was provided by Alfa Aesar and had a purity of 99.7%. Basic principles behind the heat flux method have been described in detail in many previous publications, e.g. [18–24]; therefore only specific features of the present measurements will be discussed. Schematic of the experimental setup employed in the present study was originally depicted in [20] with the latest modifications shown and described by Christensen et al. [21]. Design of the heat flux burner was essentially the same as introduced by Bosschaart and de Goey [18] with cross-section and technical details of the burner head and of the burner plate presented recently in [22,23].

All heat flux burners employed so far in our and other laboratories are made of brass; hence the main challenge of measuring the burning velocity was the corrosiveness of acetic acid towards the burner material. Although acetic acid is relatively weak, it is well known that it may react with brass [25], copper [26], bronze and similar metals producing patina on the surface. Thus it was expected that the burner exposed to acetic acid could be spoiled. For this reason the burner with the worst characteristics (significant asymmetry in the temperature profile) designated as burner "E2" by Alekseev et al. [19] was employed. This burner previously has been used in a "surface area" experiment. As described in [19], some of the holes of the burner plate close to its edge were covered with thermal paste in order to investigate how a decrease of the surface area affects the measured laminar burning velocity of methane. It should be emphasized though that the holes were cleaned from the thermal paste prior to the start of the present experiments. Nevertheless, the burning velocities of methane measured prior to the acetic acid experiments were found significantly lower (by 4.5 cm/s at stoichiometric conditions) than the results of the reference burner (burner "TS" [19]) as illustrated in Supplemental material, Fig. S1. The reference burner was evaluated to have an uncertainty below $\pm$ 0.5 cm/s [19]. Two factors may contribute to this difference. First, the burner "E2", even before any modification, showed burning velocities by 1–2 cm/s lower than the reference burner [19] and therefore was not used in our published experiments. Second, although the burner holes cleaned from the thermal paste were visually open, some residual material may reduce the effective hole size and thus modify the overall effective surface area of the burner plate.

To circumvent the limitations described above the following procedure was adopted: before each measurement series with acetic acid the burning velocity of methane + air was measured. The laminar burning velocity was determined at 298 K and equivalence ratios 0.7–1.3. The "real" burning velocity of acetic acid + air was then recalculated from the measured value by the ratio of the reference burning velocity of CH_4 and of that measured on the burner "E2": $S_{L\ real} = S_{L\ acid} * S_{L\ CH_4\ ref} / S_{L\ CH_4\ E2}$. This procedure turned out to be even more important for the data processing because it was observed that the laminar burning velocity of both CH_4 and of acetic acid was slightly lower each experimental day as illustrated in Supplemental material, Fig. S1. Nevertheless, the procedure of S_L recalculation using two values of the methane burning velocity brought consistent results when comparing measurements performed on two different setups and for the measurements repeated on the same setup after several days, as will be shown in Results section. After each experimental session the installation was flushed with ethanol and the flames of ethanol were also controlled. They behave similarly to the flames of methane with day-to-day variations and significantly lower values of S_L on the burner "E2". Methane flames were preferred as the reference for recalculation since they are investigated in many laboratories and their burning velocities are well established.

After finalizing the experiments with acetic acid the burner "E2" was disassembled and a green oxidation layer, patina, was found covering the insides of the plenum chamber and the burner head as illustrated in Supplemental material, Figs. S2 and S3. One may conclude that some portion of acetic acid reacted with the inside surface of the burner, as expected. To evaluate the impact of the surface reactions on the burning velocity experiments, an attempt to measure its products was made. With a typical flow of acetic acid + air mixture through the burner, yet without a flame, the gases were collected using a funnel placed above the burner plate and analyzed by a commercial flue gas analyzer (Varioplus Industrial). No CO_2 was detected (detection limit is 5000 ppm), while single digit ppm levels of CO were measured. Therefore the modification of the fresh mixture composition due to the surface reactions could be neglected. It is also important to note that in the experiments of Leplat and Vandooren [11] the burner was made of brass as well. Yet, no noticeable consumption of acetic acid or formation of unexpected products close to the burner surface was reported.

The measurements of the burning velocity of acetic acid + air flames span over 3 non-consecutive days using two different heat flux setups described earlier [24], yet with the same burner "E2".