Experimental and numerical study of the structure of premixed H$_2$/CO/O$_2$/Ar flames at atmospheric pressure

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Abstract. Elaboration of a predictive and well validated kinetic mechanism for combustion of H$_2$/CO mixtures is the key to development of advanced technologies for effective syngas burning in power generation systems. Moreover, understanding the combustion chemistry of H$_2$/CO mixtures is a prerequisite for a comprehensive description of hydrocarbons chemistry and development of predictive chemical kinetic models for combustion of transportation fuels. In this work we report new experimental data for chemical specification in the atmospheric pressure burner-stabilized premixed flames diluted with Ar and fuelled with H$_2$/CO (1:1) mixture at equivalence ratios of 1 and 2. Flame sampling molecular beam mass spectrometry with soft electron ionization was used to examine the flames. Recent detailed chemical kinetic mechanisms for syngas combustion available from literature were used to simulate the experimental profiles with the CHEMKIN code. A compact kinetic mechanism including 11 species and 16 reactions was elaborated to reproduce the experimental data.

1. Introduction

Coal and oil are the most important sources of energy; they are used as fuel directly in vehicles and for power generation. Due to growing concerns about environmental pollution, many countries have introduced the laws restricting emissions. Recently, thanks to the development of IGCC (Integrated Gasification Combined Cycle) technology [1,2], syngas has attracted increasing attention as an environmentally safe alternative fuel. It can be obtained not only from fossil fuels, but even from organic waste and refinery waste. Due to the difference in fuel resources and processing conditions, the composition of the syngas is diverse, in addition to the main components of H$_2$ and CO (in various ratios), it may include CO$_2$, N$_2$, CH$_4$ and other components, such as H$_2$S. The variability of the composition complicates the design of combustion devices. A change in composition significantly affects the main fuel characteristics: propagation limits [3], ignition delay times [4, 5] and laminar flame speed [6].

Understanding the combustion chemistry of H$_2$/CO mixtures is a prerequisite for a comprehensive description of the chemistry of hydrocarbons and development of predictive chemical kinetic models for combustion of transportation fuels. Despite extensive experimental efforts to examine combustion characteristics of syngas and therefore validate available chemical kinetic models for syngas combustion, there is a lack of experimental data on the concentrations of intermediates in flame conditions, in particular, at pressures close to atmospheric. In our recent work we succeeded in...
measurements of many intermediates, including O, OH, HO₂ radicals, in a stoichiometric premixed burner-stabilized H₂/CO/O₂/Ar flame at 5 atm [7]. However, working at the elevated pressure, we encountered difficulties to stabilize the H₂/CO flame in the range of equivalence ratios, so the experimental data were reported only for the stoichiometric flame.

In this work we report new experimental data for chemical speciation in the atmospheric pressure burner-stabilized premixed flames diluted with Ar and fuelled with H₂/CO (1:1) mixture at equivalence ratios of 1 and 2. In atmospheric pressure conditions we were able to span a wide range of equivalence ratios and therefore to reveal the tendencies observed with the change in the unburnt mixture composition. The goal was to ascertain how the available models for syngas combustion reproduce these tendencies, particularly for labile flame intermediates. Moreover, a compact kinetic mechanism was elaborated in this work to reproduce the novel experimental data.

2. Experimental and Modelling details
The flames of H₂/CO/O₂/Ar mixtures studied in this work were stabilized at atmospheric pressure on a Botha–Spalding burner (with perforated matrix of 16 mm in diameter), which has been used in our previous studies, see, e.g., [8]. The temperature of the burner was maintained at 95 °C by water circulating through the water jacket of the burner. Pure gases (Ar, O₂, H₂, CO) were supplied into the gas feeding line of the burner. The flow rates of the gases were regulated by mass flow controllers (MKS Instruments Inc.). The line connecting the steel bottle containing CO with the mass flow controller was partly equipped by heating element. It maintained the temperature of about 250 °C in order to provide decomposition of trace amounts of iron pentacarbonyl, which potentially could be formed in the steel bottle. The unburnt mixtures had the following molar composition: H₂/CO/O₂/Ar=0.083/0.083/0.083/0.75 (stoichiometric) and H₂/CO/O₂/Ar=0.1/0.1/0.05/0.75 (fuel-rich). Their total flow rates through the burner was 40 and 67 ml/s (at 1 atm and 25°C), respectively.

Flame sampling molecular beam mass spectrometric (MBMS) facility with soft electron ionization was used to measure spatial variations of intensities of mass peaks corresponding to various flame species. The MBMS setup has been described in detail in our previous works, see, e.g., [8]. A quartz sampling probe with the opening angle of 40º and the orifice of 50 μm was used in the experiments.

The ionization energies were set individually for each species measured. For a particular species, it must be, on the one hand, higher than the ionization energy of the species and, on the other hand, not too high to prevent the contribution to the measured mass peak of the fragment ions from other compounds. The mass peaks corresponding to H, H₂, O, OH, HCO, HO₂ were measured at 16.65 eV; water and carbon dioxide peaks were measured at 15.4 eV; CO, O₂ and H₂O were measured at 14.35 eV; and argon was measured at 16.2 eV. The mass peak signal intensities were converted to mole fractions using a procedure described earlier [8-9]. The following methods of calibration were used: direct calibration (H₂, CO, O₂, H₂O₂, CO₂), a method based on solution of O-, C-, and H-balance equations (H₂, CO, CO₂, H₂O), and the relative ionization cross-section (RICS) method (H, O, OH, HCO, HO₂). The RICS-method is described in details in [9]. The uncertainties in determining the mole fractions were as follows: ± 15% for H₂, CO, O₂, H₂O, CO₂, and for other species the mole fractions were determined to within a factor of about 2. The temperature profile in the flame was measured using a Pt-Pt + 10%Rh thermocouple made of wire 50 μm in diameter.

Numerical simulations of the flames were carried out using the PREMIX code [10]. The calculations were performed using the measured temperature profiles as input data. The numerical simulations were performed with two detailed chemical kinetic mechanisms: Goswami et al. [11] (16 species, 52 reactions) and Varga et al. (ELTE mechanism) [12] (15 species, 44 reactions). Furthermore, a compact mechanism was developed by reduction of the detailed mechanism proposed by ELTE group. The Mechanism Workbench integrated software (Kintech Lab) [13] was used for the mechanism reduction. The mechanism reduction algorithm is iterative and implements an optimal sequence of application of the following mechanisms reduction techniques: Directed Relation Graph (DRG), Rate of Production (ROP), and Computational Singular Perturbation (CSP) [14]. The resultant short mechanism included 11 species and 16 reactions among them.
Figure 1. Temperature profiles measured in the flames.

3. Results and Discussion

Figure 1 shows temperature profiles measured in both flames in the presence of the sampling probe. These profiles were used for the simulations of the flame species mole fractions. During the measurements, the junction of the thermocouple was located at 0.2 mm from the tip of the sampling probe. As is seen, the stoichiometric flame zone is slightly narrower than that of the fuel-rich one.

Mole fraction profiles of all species measured in stoichiometric and fuel-rich flames are demonstrated in Fig. 2 and 3, respectively. In these figures, the experimental data are compared with those calculated with two detailed mechanisms and the short mechanism developed in this work. As seen, mole fraction profiles of major flame species, like H$_2$, CO, CO$_2$, O$_2$ and H$_2$O in both flames are predicted by the mechanisms, including the short one, quite accurately in both flames.

In the stoichiometric flame (Fig. 2), we could measure only two intermediates: hydrogen peroxide and HO$_2$ radical. It is worthy of note that all models do not predict their mole fractions adequately. In particular, calculated mole fractions of these species near the burner surface have the highest values in the flame, whereas the experimental data show that their peaks are located at about 0.5 mm above the burner. Furthermore, the short mechanism does not include H$_2$O$_2$, and this, most likely, is the reason of the fact that the compact mechanism predicts significantly higher mole fraction of HO$_2$ at the burner surface, as compared to original ELTE model.

Figure 2. Mole fraction profiles of species measured in the stoichiometric flame.

In the fuel-rich flame (Fig. 3), we succeeded in detecting many flame intermediates, like H, OH, O, HO$_2$, H$_2$O$_2$ and HCO. As seen, short mechanism and ELTE model predict H, OH and O mole fraction profiles very well. Interestingly that ELTE model predicts additional peak of OH close to the burner
surface. This behavior of OH mole fraction is inherited by the short model. However, the experimental OH mole fraction profile exhibits only one peak of OH at ~1.2 mm above the burner. Since the short model does not include H$_2$O$_2$, HO$_2$ peak mole fraction is overpredicted by this mechanism, similarly as in the stoichiometric flame. However, in general, one can conclude that in fuel-rich conditions the detailed models predict well the profiles of H$_2$O$_2$ and HO$_2$. Experimental and calculated mole fraction profiles of HCO agree with each other qualitatively, but the experimental peak mole fraction of HCO is significantly higher than the calculated values by more than one order of magnitude. We assume that this discrepancy may be related not only to the model deficiencies but also to the high uncertainty in estimation of calibration coefficient for HCO.

**Figure 3.** Mole fraction profiles of species measured in the fuel-rich flame.

**Summary**

All models tested in this work, including the short model developed, are capable to predict accurately mole fraction profiles of major species (reactants and products) in both premixed burner-stabilized flames of H$_2$/CO/O$_2$/Ar mixture. Moreover, both detailed models reproduce quite well the mole fraction profiles of the main flame radicals (H, O, OH) and peroxy species (HO$_2$ and H$_2$O$_2$) in fuel-rich conditions. However, in the stoichiometric flame, both detailed models do not predict the mole fraction profiles of peroxy species even qualitatively. Interestingly that in our previous work, in which we investigated the structure of stoichiometric H$_2$/CO/O$_2$/Ar flame stabilized at 5 atm, the model proposed by Goswami et al. [11] predicted the profiles of H$_2$O$_2$ and HO$_2$ fairly well. We assume that the discrepancy observed in this work (at 1 atm) for these species may be related to incorrect balance in the mechanisms used between the rates of the reactions of formation and consumption of HO$_2$ and H$_2$O$_2$ at atmospheric pressure. Probably, in fuel rich conditions this balance plays minor role because the concentrations of these species are lower than in stoichiometric conditions. Therefore future work is needed to analyse the chemistry of peroxy species in the flames of syngas. Furthermore, to improve the short mechanism, H$_2$O$_2$ should be included to improve prediction of peroxy species in the flames. Finally, additional efforts should be undertaken to analyse the reactions of formation and destruction of formyl radical.
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