Oxidation of H$_2$/CO$_2$ mixtures and effect of hydrogen initial concentration on the combustion of CH$_4$ and CH$_4$/CO$_2$ mixtures: Experiments and modeling

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Abstract

An experimental investigation of the oxidation of hydrogen diluted by nitrogen in presence of CO$_2$ was performed in a fused silica jet-stirred reactor (JSR) over the temperature range 800–1050 K, from fuel-lean to fuel-rich conditions and at atmospheric pressure. The mean residence time was kept constant in the experiments: 120 ms at 1 atm and 250 ms at 10 atm. The effect of variable initial concentrations of hydrogen on the combustion of methane and methane/carbon dioxide mixtures diluted by nitrogen was also experimentally studied. Concentration profiles for O$_2$, H$_2$, H$_2$O, CO, CO$_2$, CH$_2$O, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$ were measured by sonic probe sampling followed by chemical analyses (FT-IR, gas chromatography). A detailed chemical kinetic modeling of the present experiments and of the literature data (flame speed and ignition delays) was performed using a recently proposed kinetic scheme showing good agreement between the data and this modeling, and providing further validation of the kinetic model (128 species and 924 reversible reactions). Sensitivity and reaction paths analyses were used to delineate the important reactions influencing the kinetic of oxidation of the fuels in absence and in presence of additives (CO$_2$ and H$_2$). The kinetic reaction scheme proposed helps understanding the inhibiting effect of CO$_2$ on the oxidation of hydrogen and methane and should be useful for gas turbine modeling.

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1. Introduction

Significant progress has been made recently to develop new technologies (i.e. IGCC or IRCC for gas turbine applications) using H$_2$ as alternative fuel aimed at decreasing air pollution. It is recognized that the combustion of fossil fuels in air is a major factor of atmosphere CO$_2$ concentration increase, participating in global warming. Net CO$_2$ emissions can be reduced by dissolution in seas or underground storage in exhausted oil/gas wells. Furthermore, CO$_2$ removal via capture and sequestration could be facilitated if reused as a diluent in place of nitrogen in combustion [1]. Addition of hydrogen to natural gas could improve the flame stability and reduce the emission of CO$_3$ and NO$_x$ in ultra-lean combustion [2,3]. Therefore, it is important to study the effect of such compounds on the kinetics of oxidation of hydrogen and conventional fuels such as natural gas and provide a combustion kinetic model.

New experimental results obtained for the oxidation of neat hydrogen and hydrogen in presence of 30% CO$_2$ in a jet-stirred reactor (JSR) at 1 atm,
over a range of equivalence ratio (0.2–2), and for temperatures in the range 800–1050 K are presented. Experiments where different concentrations of H₂ are added to methane and methane–20% CO₂ mixtures were also performed at 1 and 10 atm. This new set of data are complementary to that already obtained with the same experimental set-up [4]. The oxidation of these fuels under JSR, shock-tube, and premixed flame conditions was modeled using a detailed kinetic scheme.

2. Experimental set-up

The JSR experimental set-up used here was presented previously [4–8]. It consisted of a 30 cm³ fused-silica sphere, to minimize wall catalytic reactions, equipped with four nozzles of 1 mm ID for the admission of the gases providing the stirring. A nitrogen flow of 0.1 m³/h was used to dilute the fuel. As before [4–8], all the gases were preheated before injection, minimizing temperature gradients inside the reactor (typically <3 K/cm along the vertical axis of the reactor by measurements using a Pt/Pt–Rh 10% thermocouple located inside a thin-wall fused-silica tube to prevent catalytic reactions on the wires of 0.1 mm in diameter). The flow rates were measured and regulated by thermal mass-flow controllers (Brooks 5850 TR and 5850E). Low-pressure samples were taken by sonic probe and collected in 1 L Pyrex bulbs at ca. 50 mbar for immediate gas chromatography analyses as in [4,7–9] using thermal conductivity and flame ionization detection. On-line Fourier transform infrared analyses were also performed by connecting the sampling probe to a temperature controlled (413 K) gas cell (2 and 10 m path length, 200 or 500 mbar) via a Teflon heated-line (Tyco) maintained at 403 K. Carbon-balance was checked for every sample and found good within 100 ± 8%.

3. Modeling

The JSR computations were performed using PSR [10]. The reaction mechanism used has a strong hierarchical structure. It is based on a comprehensive hydrocarbon oxidation mechanism [5] and consisted of 128 species and 924 reversible reactions. The rate constants for reverse reactions were computed from the corresponding forward rate constants and the equilibrium constants, \( K_c = k_{\text{forward}} / k_{\text{reverse}} \), calculated from thermochemistry [6,11,12]. This mechanism is available from the authors (dagaut@cnrs-orleans.fr) and as supplemental material. PREMIX [13] and SENKIN [14] were used to, respectively, simulate premixed flames and the ignition delays.

4. Results and discussion

The oxidation of hydrogen/N₂ and hydrogen/N₂/CO₂ mixtures was studied at 1 atm, for equivalence ratios of 0.2–2. The concentration of CO₂ was kept constant (30% in mole). This data set helped understanding the effect of CO₂ on the kinetic of hydrogen oxidation over a wide range of fuel composition in a JSR. To study the effect of hydrogen on methane/N₂ and methane/N₂/CO₂ mixtures, the experiments were performed at 1 and 10 atm, and in fuel-lean conditions (\( \phi = 0.3 \)). The concentration of CO₂ added to methane mixtures was 20%: the initial composition of oxygen was kept constant and that of hydrogen and methane were varied to maintain the equivalence ratio at 0.3 (Table 1). The reaction was studied by varying the operating temperature in the JSR stepwise. Concentration profiles for O₂, H₂, H₂O, CO, CO₂, CH₃O, CH₄, C₂H₆, C₂H₄, and C₂H₂ were measured. The mean residence time in the JSR was kept constant in the experiments: 120 ms at 1 atm and 250 ms at 10 atm.

4.1. The oxidation of hydrogen and hydrogen–CO₂ mixtures

Figures 1–4 compare the computed results and the experimental concentration profiles for the oxidation of neat hydrogen and that of hydrogen–CO₂ mixtures. As can be seen from these figures, the model represents fairly well the data for the oxidation of hydrogen. At 1 atm, hydrogen begins to oxidize at 875 K; this temperature is the same for all our neat hydrogen experiments. The initial consumption of hydrogen is due to

\[
\text{H}_2 + \text{O}_2 = \text{H}_2\text{O} + \text{H} \quad (\text{R}13) \]

As already well known, the very important reactions in the H₂–O₂ system are

\[
\text{H} + \text{O}_2 = \text{OH} + \text{O} \quad (\text{R}6) \quad \text{and} \quad \text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M} \quad (\text{R}7) \]

In the JSR at 1 atm, beside reaction R6, the OH radical is also mainly formed through

\[
\text{H}_2 + \text{O} = \text{OH} + \text{H} \quad (\text{R}5) \quad \text{and} \quad \text{H} + \text{HO}_2 = \text{OH} + \text{OH} \quad (\text{R}14) \]

which consume H and O. When 30% of N₂ is replaced by CO₂, the conversion rate of hydrogen is reduced (Figs. 1–4). In presence of CO₂, the temperature at which hydrogen starts to oxidize is shifted towards higher values (ca. +50 K). The kinetic analysis performed at 950 K for the two mixtures \( \phi = 0.2 \) and \( \phi = 2 \) shows that in presence of 30% CO₂, the rate of production of OH via R6 decreases. Actually, this OH rate of production is reduced from 27% to 18% and from 21% to 8% at, respectively, \( \phi = 0.2 \) and \( \phi = 2 \). The presence of CO₂ favors the formation of OH through

\[
\text{H}_2\text{O}_2 \quad (+\text{M}) = \text{OH} + \text{OH} \quad (+\text{M}) \quad (\text{R}18) \]

The rate of production of OH via this reaction increases from 1% to 11% for the mixture \( \phi = 0.2 \), when 30% of
CO₂ is added. This implies that, when present in the fuel, CO₂ affects the formation and decomposition of H₂O₂ via the sequence of reactions

\[ H + O_2 = OH + O \ (R6); \]

\[ H + O_2 + M = HO_2 + M \ (R7); \]

\[ 2HO_2 = H_2O_2 + O_2. \]

The importance of R7 is increased in presence of CO₂ at the expense of R6 because of the higher collision efficiency for CO₂ than for N₂ in R7. Therefore, at 950 K and
\( \varphi = 0.2 \), the mole fraction of \( \text{HO}_2 \) is increased by a factor of ca. 2, yielding an increase of the rate of \( 2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) (R16, R17) by a factor of ca. 3.6. This increase in \( \text{HO}_2 \) concentration results from a relatively lower rate of consumption of \( \text{HO}_2 \) in presence of \( \text{CO}_2 \) since (i) the reactions between \( \text{H} \) and \( \text{HO}_2 \) are less important due to the consumption of \( \text{H} \) via the reaction \( \text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH} \) (R24), and (ii) the reactions of \( \text{HO}_2 \) with \( \text{O} \) and \( \text{OH} \) are less important due to the reduced rate of R6. Reaction path analyses showed that when \( \text{CO}_2 \) is added to the hydrogen mixtures, it reacts with \( \text{H} \) radicals through \( \text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH} \) (R24). This reaction removes \( \text{H} \) radicals which are normally consumed by reactions R6 and R14. This induces a decreased production of \( \text{OH} \) by R6 in presence of \( \text{CO}_2 \) and a decreased hydrogen rate of oxidation. The inhibiting effect of \( \text{CO}_2 \) is more obvious in fuel-rich conditions. The chemical impact of \( \text{CO}_2 \) produces \( \text{CO} \) by R24 (Figs. 3 and 4). The concentration of \( \text{CO} \) produced increases with increasing \( \varphi \). Figure 5 presents the influence of fuel composition on \( \text{CO} \) formation when \( \text{CO}_2 \) is initially present in the reacting mixtures. In this case, the general trend is predicted by the present model.
model that under-predicts CO concentrations by less than 17% in the worst case.

We have simulated the oxidation of hydrogen in the JSR with variable initial concentration of CO2 (0%, 30%, 50%, and 97.5%). The results show a strong inhibition of hydrogen conversion by CO2, increasing with CO2 initial concentration (Fig. 6a). The quantity of CO produced increases with the oxidation temperature and the CO2 concentration (Fig. 6b). When CO2 is added to fuels, the thermal and transport properties of the system change due to CO2 high heat capacity and transport properties. As a result, the burning velocities are modified. Previous studies examined the effect of CO2 on hydrogen flames [15–17]. Here, the effect of CO2 dilution on burning velocities was also examined here by simulating the literature experiments (Fig. 7). The data and the modeling show the dilution by CO2 reduces the burning velocities of hydrogen–air. This reduction is explained by the competition between the reactions –R24 and R6 when CO2 is added. Because the flame speeds of hydrogen mixtures are highly sensitive to reaction R6, the decrease of this reaction rate decreases flame velocities.

Ignition delays of hydrogen/O2/Ar mixtures in presence of CO2 have been measured at a mean pressure of 1.1 atm [18]. This data set is well simulated by our model (Fig. 8). Both show that CO2 addition increases the ignition delays of hydrogen mixtures. In fact (Fig. 8) below 1000 K, the mixture 4% H2–2% O2–Ar ignites faster than the corresponding mixture with 10% CO2. However, above this temperature, the ignition delays of the two mixtures are very similar.

4.2. Effect of hydrogen initial concentration on methane and methane–CO2 oxidation

The second series of JSR experiments performed here concerns the oxidation of methane and methane–CO2 mixtures in presence of variable initial concentration of hydrogen at a temperature of 1025 K. This temperature was chosen because it is convenient to compare the oxidation of neat CH4 and CH4–H2 mixtures: at lower temperature, methane is not reacting whereas at
higher temperature, the mixture CH$_4$–H$_2$ is too reactive. The mole fractions of hydrogen ranged from 0% to 2% whereas those of methane where 1–0.5%. The initial composition of oxygen in all the mixtures was 6.67%, giving a constant equivalence ratio of 0.3. The concentration profiles were simulated (Figs. 9–12). The present modeling represents fairly well the consumption of CH$_4$ and the formation of H$_2$O, CO, CO$_2$, CH$_2$O and C$_2$H$_4$ during the oxidation of methane–hydrogen and methane–hydrogen–CO$_2$ at 1 atm.

In agreement with recent studies [19,20], the conversion of methane increases with increasing hydrogen initial concentration (Figs. 13 and 14). Due to its high reactivity, hydrogen favors the oxidation of methane. The present simulations indicated an increased production of H atoms via H$_2$ + O = OH + H (R5) and H$_2$ + OH = H$_2$O + H (R9) in presence of H$_2$, whereas the formation of H atoms yields an increased production of OH radicals via H + O$_2$ = OH + O (R6) and H + HO$_2$ = OH + OH (R14).

By increasing pressure, recombination reactions become more important; the stabilization of HO$_2$ radicals is favored and the production of OH occurs through the reaction path: H + O$_2$ + M = HO$_2$ + M (R7), HO$_2$ + HO$_2$ = H$_2$O$_2$ + O$_2$ (R16), H$_2$O$_2$ (+M) = OH + OH (+M) (−R18). The H radical is formed via CH$_3$ + H$_2$ = CH$_4$ + H (R79). Below 40% of H$_2$ in the fuel mixture (Fig. 13), the conversion of methane at 10 atm is higher than at 1 atm but above 40% of H$_2$, it is the opposite. This result can be explained by a high concentration of CH$_3$ radicals at low initial concentration of H$_2$.
in the mixtures since the formation of the H radical is favored by reaction R79. Reaction paths analyses allowed drawing a schematic of the effect of hydrogen on methane oxidation (Fig. 14).

The inhibiting effect of CO₂ on the oxidation of methane was also observed: in presence of 20% CO₂, the conversion of CH₄ decreases (Fig. 15). Reaction path analyses indicated that the chemical impact of CO₂ on CH₄ oxidation is similar to that on H₂ oxidation. The competition between reaction –R24 and reactions producing the main radicals becomes more important when CO₂ is present. In addition to the inhibiting effect, CO₂ favors the formation of C₂-hydrocarbons, especially C₂H₄ here. Figure 16 compares the C₂H₄ concentration profiles from the oxidation of mixtures containing or not CO₂. The concentration of C₂H₄ produced with CO₂ present is higher than without CO₂, particularly in the higher reactivity zone (high initial hydrogen concentration).

Previous studies indicated the presence of hydrogen in the fuel increases laminar flame speeds [21–24]. The proposed model agrees with the recent data taken from the literature [24]. The laminar burning velocities of CH₄–H₂–CO₂ flames reported in [25,26] were simulated (Fig. 17). The proposed model represents well the data whereas that of [27] slightly under-predicts the reactivity of the mixture containing 35% hydrogen.

5. Conclusion

The two main objectives of the present study were achieved: (i) a large data set, consisting of concentration profiles of reactants, stable intermediates and products, was obtained for the oxidation of hydrogen- and methane-based fuels (H₂, CH₄, H₂/CO₂, CH₄/CO₂, CH₃/H₂/CO₂) in a JSR at 1–10 atm, over the temperature range
800–1050 K, from fuel-lean to fuel-rich conditions; (ii) a kinetic modeling was performed generally yielding a good agreement with the present data and the literature data (burning velocities, ignition delays) further validating our kinetic scheme. The results show that CO2 inhibits the oxidation of H2 and the conversion of methane increases with the increase in hydrogen initial mole fraction. Reaction paths analyses were used to delineate the important reactions influencing the kinetic of oxidation of the fuels in presence of CO2 and H2. They indicated (1) the effect of CO2 addition under JSR conditions mainly results from the competition between the reaction CO2 + H = CO + OH and reactions producing important radicals, (2) the production of H and OH in presence of hydrogen in methane mixtures is mainly due to reactions in the H2–O2 system, and (3) when hydrogen is added to methane at high pressure, H radicals are also produced by the reaction CH3 + H2 = CH4 + H, and the formation of OH radicals is favored by the decomposition of H2O2. In flames, the increased concentration of H2 yields higher flame speeds and the dilution by CO2 yields lower burning velocities of fuel mixtures.

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Appendix A. Supplement material

Reaction mechanism and thermochemistry, experimental data are provided as supplementary material. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.proci.2008.05.079.

References


