Chapter 7

The effect of hydrogen addition to rich stabilized methane/air flames
7.1 Introduction

Stringent emission regulations for greenhouse gases and the drive to conserve the finite supplies of fossil fuels have resulted in increased interest in the possible addition of sustainable hydrogen to natural gas. In spite of any potential advantage to hydrogen addition in this regard, a negative effect on other aspects of combustion performance, such as increased pollutant emissions (NOx, soot), must be weighed in the overall considerations. Recently, several studies on the effect of hydrogen addition to hydrocarbons have been conducted regarding extinction limits [1], burning velocities [2-4] and engine performance [5]. However, very few flame structure studies have been performed on hydrogen-hydrocarbon mixtures, and all of these pertained to non-premixed flames. For example, the effect of hydrogen was studied in a hydrogen-natural-gas composite fuel in turbulent jet flames [6], and showed that increasing the hydrogen concentration resulted in an increase in soot, CO and NOx formation. Another study [7] added natural gas and propane to coflow hydrogen diffusion flames; a decrease in soot formation and an increase in NOx with increasing hydrogen content were found. In the same type of flames, intermediate radicals were measured [8,9] and a decrease in CH radical concentration was observed with increasing hydrogen content. In these studies, the increase in NOx emission was ascribed to the increasing flame temperature with hydrogen content, which promotes thermal NOx production. However, the measured decrease in CH concentration with hydrogen content suggests that hydrogen addition to hydrocarbon flames reduces the NOx emissions contributed from the Fenimore mechanism. The analysis of the chemistry in the coflow diffusion flame studies described above suffers from the complication of multidimensional transport and the fact that the difference in diffusive behavior between the relative heavy hydrocarbon fuels and hydrogen is very large. For this reason, measurements of key intermediates species in pollutant formation using premixed one-dimensional flames can yield a more unambiguous contribution to understanding the consequences of hydrogen addition for the chemistry of pollutant formation. To date, no quantitative studies have been reported on the effect of hydrogen addition on pollutant formation in one-dimensional flames.

One of the key intermediate species in the formation of soot in rich hydrocarbon flames is acetylene [10] and understanding the fate of this species is essential to understand soot inception. Also, acetylene is a precursor of the CH radical [11], which
is an important intermediate in Fenimore NO formation in hydrocarbon flames [12]. As discussed in chapter 6, HCN is an important intermediate in the Fenimore mechanism as well. Moreover, due to the lack of oxygen radicals in fuel-rich flames the conversion of HCN to NO is slow and the poisonous HCN can survive in the post-flame gases (chapter 6). As mentioned in chapter 5 and 6, and reference therein, both acetylene and HCN have been investigated in flat, atmospheric-pressure premixed hydrocarbon flames. However, to our knowledge no quantitative studies have been reported of the effects of hydrogen addition on the formation and destruction of C₂H₂ and HCN in premixed CH₄/air flames. Since there are substantial concentrations of HCN and C₂H₂ in rich premixed flames, we study these effects in flames similar to those discussed in chapter 5 and 6. Towards this end we measured the profiles of C₂H₂ and HCN in rich-premixed H₂/CH₄/air flames at atmospheric pressure. The technique used is microprobe gas sampling followed by analyses using tunable diode laser absorption spectroscopy and wavelength modulation absorption spectroscopy with second harmonic detection (chapter 4). In addition, the experimental observations are compared with one-dimensional flame calculations.
7.2 Experimental

The flat, atmospheric-pressure premixed flames of CH$_4$/H$_2$/air have been stabilized on a 6-cm diameter flat-flame water-cooled Mc-Kenna Products burner and surrounded by a coflow of nitrogen to prevent from mixing with ambient air (chapter 4). The experimental conditions are summarized in table 7.1.

Table 7.1. Flame parameters

<table>
<thead>
<tr>
<th>Flame</th>
<th>$\varphi$</th>
<th>H$_2$ (%)</th>
<th>$\rho v$, g/cm$^2$·s</th>
<th>$T$, K (GRI-3.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5</td>
<td>0</td>
<td>0.005</td>
<td>1760</td>
</tr>
<tr>
<td>B</td>
<td>1.5</td>
<td>23</td>
<td>0.005</td>
<td>1740</td>
</tr>
<tr>
<td>C</td>
<td>1.3</td>
<td>0</td>
<td>0.005</td>
<td>1763</td>
</tr>
<tr>
<td>D</td>
<td>1.3</td>
<td>23</td>
<td>0.005</td>
<td>1743</td>
</tr>
<tr>
<td>E</td>
<td>1.4</td>
<td>0</td>
<td>0.008</td>
<td>1854</td>
</tr>
<tr>
<td>F</td>
<td>1.4</td>
<td>20</td>
<td>0.008</td>
<td>1833</td>
</tr>
<tr>
<td>G</td>
<td>1.4</td>
<td>50</td>
<td>0.010</td>
<td>1834</td>
</tr>
<tr>
<td>H</td>
<td>1.4</td>
<td>50</td>
<td>0.008</td>
<td>1797</td>
</tr>
<tr>
<td>I</td>
<td>1.5</td>
<td>0</td>
<td>0.008</td>
<td>1848</td>
</tr>
<tr>
<td>J</td>
<td>1.5</td>
<td>20</td>
<td>0.008</td>
<td>1829</td>
</tr>
<tr>
<td>K</td>
<td>1.5</td>
<td>50</td>
<td>0.008</td>
<td>1796</td>
</tr>
</tbody>
</table>

Measurements were obtained at different vertical positions in the flame by moving the burner with a precision positioner up to a distance of 10 mm in steps of 1 mm. As was done in the previous chapters, all measured HCN and C$_2$H$_2$ concentration profiles are shifted 1.3 mm upstream to correct for the probe distortion. The methods for obtaining the C$_2$H$_2$ and HCN mole fractions, via tunable diode laser absorption spectroscopy are described in detail in chapter 4.

Given the excellent predictive power of Chemkin II [13] with GRI-Mech 3.0 [14] for predicting the flame temperature observed in chapter 5 for methane/air flames, and in other studies in methane/air [15] and hydrogen/air flames [16], calculated flame temperatures were used in this study (Table 7.1). Calculations were
performed by using the measured mass flux through the burner surface as an input parameter.

### 7.3 Results and discussion

The addition of hydrogen to the unburned methane/air mixture changes the flame properties. The laminar flame velocity of pure hydrogen is 8 times higher than that of pure methane [4]; we thus expect that the flame velocity of methane to increase substantially upon hydrogen addition. When the flame is stabilized above the burner surface, we expect hydrogen addition to cause a significant temperature reduction; at constant mass flux through the burner, the higher flame velocity should result in more heat transfer to the burner. To illustrate this, figure 7.1 presents the calculated flame temperature as function of the mass flux for methane and a methane/hydrogen mixture. As can be seen, replacement of 50% methane by hydrogen results, at constant mass flux, in a substantial decrease in the calculated flame temperature, caused by increased heat transfer to the burner.

![Figure 7.1. Calculated flame temperature as function of the mass flux for a pure methane (solid line) and a methane/hydrogen, 50/50 mixture (dashed line), both having an equivalence ratio of ϕ=1.5.](image)

Figure 7.1. Calculated flame temperature as function of the mass flux for a pure methane (solid line) and a methane/hydrogen, 50/50 mixture (dashed line), both having an equivalence ratio of ϕ=1.5.
7.3.1 HCN profiles

To study the effect of hydrogen addition to fuel-rich CH₄/air flames on the formation and consumption of HCN, several flames with different equivalence ratios (ϕ=1.3, 1.4 and 1.5) and hydrogen concentrations in the fuel mixture (0%, 20% and 50% by volume) have been studied (see Table 7.1). For the flames at ϕ=1.5 (flames I-K) and ϕ=1.4 (flames E, F, H) the mass flux is kept constant with different hydrogen content in the mixture. As expected from figure 7.1, hydrogen addition to the methane/air mixtures while keeping the mass flux constant decreases the flame temperature (I-K and E, H) slightly (see also Table 7.1). For the flames with equivalence ratio ϕ=1.4 (flames E-G), the temperature was kept more or less constant (±20K) by increasing the mass flux when more hydrogen was added.

The experimental profiles of HCN mole fraction in Figs. 7.2 and 7.3, for ϕ=1.4 and ϕ=1.5, respectively, show that as the fraction of hydrogen in the fuel mixture increases, the HCN mole fraction decreases substantially, well outside the measurement uncertainty. For example, increasing the hydrogen content in the fuel from 0 to 50% lowers the HCN mole fraction by more than a factor of two, at both equivalence ratios. According to reaction (R6.1) in Chapter 6, HCN should be linearly related to the CH and N₂ concentration. Furthermore, one could make the simple “naïve” assumption that CH is directly proportional to the CH₄ concentration in the fuel/air mixture. Following this simple line of thought, replacing 20% (v/v) methane by hydrogen in the fuel results in a reduction, by “dilution”, in the CH₄ mole fraction by ~7% and ~2% in the N₂ mole fraction in the fuel-air mixture; taken together this would in turn decreases the HCN concentration via reaction R6.1 by ~10%. When increasing the hydrogen fraction to 50% a HCN decrease of ~30% could thus be expected. That a factor of 2 decrease in HCN is observed for a hydrogen fraction of 50%, suggests an additional effect, besides dilution, on flame structure. Figure 7.2 shows, for the flames with 50% hydrogen addition (flames D and J), that lowering the temperature by ~60 K does not affect the HCN peak concentration significantly, as also seen for the “pure” methane/air flames in chapter 6. Interesting to note in figures 7.2 and 7.3 is that at constant mass flux the HCN peak concentrations appears to shift towards the burner surface as the fraction of hydrogen in the fuel increases from 0 to 50%, indicative of the higher degree of burner stabilisation caused by the increased burning velocity.
Figure 7.2. Axial profiles of HCN mole fraction in CH₄/air flames and CH₄/H₂/air flames, ϕ = 1.4. Symbols denote probe measurements in flames E (squares), F (diamonds), G (circles) and H (triangles). The lines denote flame calculations using GRI-Mech 3.0 in flames E (dashed), F (dotted) G (bold solid) and H (thin solid).

Figure 7.3. Axial profiles of HCN mole fraction in CH₄/air flames and CH₄/H₂/air flames, ϕ = 1.5. Symbols denote probe measurements in flames I (diamonds), J (squares) and K (triangles). The solid lines denote flame calculations using GRI-Mech 3.0 in flames I (dashed), J (solid) and K (dotted).
Comparison of the calculated and measured HCN concentration profiles at $\varphi=1.4$ (figure 7.1) shows for all flames substantial overprediction of the HCN peak concentration and significant slower HCN decay relative to the experimental results, similar to those observed in Chapter 6 for the pure methane fuel. Moreover, whereas a reduction in the measured HCN peak concentration at $\varphi=1.4$ is related to the amount of hydrogen addition, with only a modest effect of temperature, the calculations suggest that the HCN reduction is mainly related to the flame temperature and not due to a “hydrogen” effect. For example, increasing the hydrogen content from 20% (flame F) to 50% (flame G) at constant flame temperature does not reduce the maximum calculated HCN concentration, but lowering the flame temperature while keeping 50% hydrogen content in the fuel (flame H) results in a substantial reduction in the calculated HCN peak concentration. Although it is tempting to further interpret the calculations, we note that these observations are in contradiction with the measurements. It is thus not prudent to pursue the analysis using GRI-Mech 3.0. A possible explanation for the large quantitative and qualitative discrepancies between calculated and measured HCN peak concentrations observed at $\varphi=1.4$ (figure 7.2) is that in GRI Mech 3.0 the temperature sensitive reaction $\text{CH+N}_2=\text{HCN+N}$ (R6.1, chapter 6) is the main source of formation of HCN, while as discussed in Chapter 6 recent theoretical studies [17,18] point to NCN and not HCN as the primary product of this reaction.

In contrast to the poor agreement at $\varphi=1.4$, figure 7.3 shows for the flames studied at $\varphi=1.5$ moderately good agreement between measured and calculated HCN profiles. However, as observed above, the calculations are very sensitive to burner stabilization, as reflected in the flame temperature, and we ascribe the “good” agreement with the trend observed here for $\varphi=1.5$ as a spurious effect of the changes in flame temperature. This “temperature” effect is even more dramatically illustrated in figure 6.3; where the experimental profiles differ only modestly for a change in flame temperature of $\sim 100$ K, while the calculations change by a factor of 3. Due to the significant quantitative discrepancies between calculated and measured HCN profiles observed at $\varphi=1.4$ (figure 7.2), and for the spurious effect of temperature observed at $\varphi=1.5$ in Chapter 6 (figure 6.3), and suspected in figure 7.3, we refrain from the further mechanistic analyse the effect of hydrogen on the HCN mole fraction. Based on the results reported here, a reanalysis of the chemical mechanism is
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deemed necessary. To do so, detailed information on the NCN kinetics is must be obtained. We hope that the experimental data presented here will be useful in performing this task.

7.3.2 C2H2 profiles

The effect of replacing 23% methane by hydrogen, at constant mass flux, on the C2H2 profiles is illustrated in figure 7.4. The results show for equivalence ratios 1.3 and 1.5 (Flames A-D in Table 1) that H2 addition only slightly decreases the measured peak C2H2 mole fraction. This small reduction of C2H2 is essentially the same as the ~15% decrease “naively” expected from dilution when 23% methane is replaced by hydrogen, here too making the simple assumption that C2H2 formation is directly proportional to the concentration of hydrocarbons in the fuel. No substantial difference in the measured C2H2 concentration is observed in the post flame zone for the flames with (B, D) and without hydrogen addition (A, C).

In addition, the predicted C2H2 profiles obtained using GRI-Mech 3.0 are compared with the measurements. As can be seen from figure 7.4, the calculated C2H2 profile (dashed line) shows substantially higher peak concentrations and slower decay in the post flame zone for flame D. Although not presented, the computed C2H2 profiles for the other flames shown in figure 7.4 show similar discrepancies, as expected from the results presented in Chapter 5 and in Ref. [19]. Replacing the rate coefficient of the reaction C2H2 + OH → CH2CO +H used in the GRI 3.0 mechanism by the expression 4.87 x 10^{13}\exp(-12000\text{cal}/RT) \text{cm}^3\text{mol}^{-1}\text{s}^{-1} recommended in chapter 5 yields very good agreement between measurements and calculations for all flames studied, as can be seen in the figure.
Figure 7.4. Axial profiles of HCN mole fraction in CH4/air flames and CH4/H2/air flames, $\varphi = 1.5$ and 1.3. Symbols denote probe measurements in flames A (circles), B (squares), C (diamonds) and D (triangles). The dashed line denotes flame the calculation with GRI-3.0, and other lines, flame A (bold solid lines), flame B (thin solid line), flame C (bold doted line) and flame D (thin dotted line) are the result of calculations with the increased rate coefficient for $C_2H_2+OH \rightarrow CH_2CO+H$.

7.4 Conclusion

In this chapter we examined the effect of hydrogen addition on the formation and destruction of HCN and $C_2H_2$ in rich premixed CH4/air mixtures. The HCN measurements at equivalence ratios $\varphi=1.4$ and 1.5 show that the HCN mole fraction decreases substantially with increasing hydrogen content in the fuel mixture. This decrease significantly exceeds the reduction in HCN expected from the dilution of the hydrocarbon fuel and nitrogen when hydrogen is added to the mixture, suggesting that addition of hydrogen affects the flame structure related to the formation of HCN. In contradiction to the measurements, calculations, using GRI-Mech 3.0 show at $\varphi=1.4$ and constant flame temperature no substantial reduction in the HCN peak concentration when hydrogen is added to the mixture, while a reduction in flame temperature results in a substantial decrease in the calculated HCN peak concentration at the same hydrogen fraction in the fuel (50% v/v). Moreover, calculations predict substantially higher HCN peak mole fractions and slower oxidation in the post flame
zone as compared to the measurements for all flames at $\varphi=1.4$. Increasing the hydrogen content in the fuel for the flames at $\varphi=1.5$ results in roughly the same systematic decrease in the calculated HCN concentration as measured. However, this observed reduction is probably caused by the reduction in temperature caused by increased stabilization, which is not supported by the measurements presented in this thesis, and not due to a “hydrogen effect”.

The $C_2H_2$ measurements show that the addition of 23% hydrogen results in only a marginal reduction of the $C_2H_2$ concentration for the flames measured at $\varphi=1.3$ and 1.5, suggesting that hydrogen addition does not have any significant effect on the flame processes responsible for $C_2H_2$ formation/consumption in CH$_4$/air flames. Comparison between calculated and measured profiles shows significant overprediction of the maximum $C_2H_2$ concentration and a much slower predicted decay of $C_2H_2$ in the post flame zone. As expected from Chapter 5, replacing the rate coefficient of the reaction $C_2H_2 + OH \rightarrow CH_2CO + H$ used in the GRI-Mech 3.0 mechanism by $4.87 \times 10^{13}\exp(-12000\text{cal/RT})$ cm$^3$mol$^{-1}$s$^{-1}$ resulted in good agreement between measured and calculated $C_2H_2$ profiles for all flames studied.
7.5 Literature
