Chapter 4

The Effects of Burner Stabilization on Fenimore NO Formation in Low-Pressure, Fuel-Rich Premixed CH$_4$/O$_2$/N$_2$ Flames
4.1 Introduction

As discussed in Chapter 1, experiments at low pressure are necessary to elucidate the changes in flame structure that are responsible for the variation in NO formation in fuel-rich flames upon varying the degree of stabilization. A number of studies have been performed that provide insight into the Fenimore mechanism in low-pressure methane flames under fuel-rich conditions [1-4]. As a result, valuable information has been obtained for use in assessing the rates of important elementary reactions [1-3], and interesting insights into the effects of ethane and propane addition on NO chemistry in methane flames [4] has been gained. These reports, however, have been restricted to \( \phi < 1.3 \), and the effects of varying burner stabilization remain yet unexamined. In this Chapter, we specifically examine the effects of burner stabilization on Fenimore NO formation in low-pressure fuel-rich (\( \phi = 1.3-1.5 \)) methane/oxygen/nitrogen flames. Towards this end, we measure the profiles of temperature, and mole fractions of OH, CH and NO, using the experimental methods for quantitative laser-induced fluorescence described in detail in Chapter 3. Since this parameter variation represents a substantial extension to the previous studies, we also use the results to test predictions calculated using GRI-Mech 3.0 [5].

4.2 Experimental details

Twelve premixed flames are studied between \( \phi = 1.3-1.5 \) for which the conditions are summarized in Table 4.1. The flames are stabilized on a water-cooled 6 cm McKenna Products burner located inside the low pressure chamber as described in Chapter 2.
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<table>
<thead>
<tr>
<th>Flame(^a)</th>
<th>(\phi)</th>
<th>(T_{\text{max\ exp}}) (K)</th>
<th>(T_{\text{ad}}) (K)</th>
<th>(X_{\text{CH\ exp}}) (ppm)</th>
<th>(X_{\text{NO\ exp}}) (ppm)</th>
<th>(X_{\text{NO\ calc}}) (ppm)</th>
<th>(X_{\text{NO,Fen}}) (ppm)</th>
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<tr>
<td>A1</td>
<td></td>
<td>2000</td>
<td>2150</td>
<td>19.0</td>
<td>40.2 ± 6.0</td>
<td>39.6</td>
<td>38.3</td>
</tr>
<tr>
<td>A2</td>
<td>1.3(^b)</td>
<td>2150</td>
<td>2393</td>
<td>30.5</td>
<td>50.3 ± 7.5</td>
<td>48.8</td>
<td>48.8</td>
</tr>
<tr>
<td>A3</td>
<td></td>
<td>2285</td>
<td>2200</td>
<td>37.4</td>
<td>63.4 ± 9.5</td>
<td>63.0</td>
<td>63.6</td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td>1935</td>
<td>2090</td>
<td>18.8</td>
<td>33.0 ± 5.0</td>
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<tr>
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<td>2090</td>
<td>2469</td>
<td>24.5</td>
<td>40.9 ± 6.1</td>
<td>44.2</td>
<td>45.3</td>
</tr>
<tr>
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<td></td>
<td>2200</td>
<td>2200</td>
<td>35.4</td>
<td>51.5 ± 7.7</td>
<td>53.6</td>
<td>50.1</td>
</tr>
<tr>
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<td></td>
<td>2020</td>
<td>2140</td>
<td>14.7</td>
<td>37.4 ± 5.6</td>
<td>54.1</td>
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</tr>
<tr>
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<td>2140</td>
<td>2442</td>
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<td>59.2 ± 8.9</td>
<td>77.1</td>
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<tr>
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<td></td>
<td>2080</td>
<td>2220</td>
<td>15.5</td>
<td>40.0 ± 6.0</td>
<td>60.8</td>
<td>53.4</td>
</tr>
<tr>
<td>D2</td>
<td>1.5(^c)</td>
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<td>2400</td>
<td>23.2</td>
<td>54.0 ± 8.1</td>
<td>95.8</td>
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<tr>
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<td>2295</td>
<td>32.5</td>
<td>64.2 ± 9.6</td>
<td>99.6</td>
<td>72.0</td>
</tr>
</tbody>
</table>

Reference flame\(^e\) 1.07 1920 2344

\(^a\) The total flows are 3, 4 and 5 slpm for the flames denoted “1”, “2” and “3” respectively, except for the “reference” flame where the total flow is 3.2 slpm (1 slpm corresponds to ~0.0007 g/cm\(^2\)s). \(^b\) \(p = 25\) Torr and \([O_2]/[N_2]+[O_2]=0.35\), \(^c\) \(p = 35\) torr and \([O_2]/[N_2]+[O_2]=0.40\), \(^d\) At axial distance of 1.6 cm \(^e\) Flame conditions are identical to Berg et al. [3]standard flame.

Table 4.1 Flame conditions and data from CH and NO measurements (see text for details)

4.3 Results and discussion

4.3.1 Temperature and OH profiles

The profiles of temperature and OH mole fraction measured in the 25 torr, \(\phi = 1.3\) flames (Flames A1, 3 l/min, and A3, 5 l/m) are shown in Figure 4.1, and are typical for the measurements presented. The error bars shown are the uncertainties given in Chapter 3.
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Figure 4.1 OH and temperature profiles for Flames A1 (3 l/min) and A3 (5 l/min). Points denote measurements. Open symbols are temperature profiles; corresponding lines are empirical fits to the measurements (see Chapter 3). Filled symbols are OH mole fractions; corresponding lines are predictions from GRI-Mech 3.0. Triangles refer to A1, squares to A3.

After the initial rise in the flame front, the temperature profiles for all flow rates are flat within the uncertainty of the measurements. Both temperature and OH mole fraction grow with increasing flow rate of the cold gases, as is to be expected from the decreasing heat loss necessary to stabilize the flame [6]. We note that the OH mole fraction decreases by nearly a factor of two with the decrease in temperature of nearly 300 K upon decreasing the flow rate from 5 to 3 l/min. Figure 4.1 also shows the calculated OH profiles using the temperature fits from equation (3.19) (shown as lines in the Figure) as constraints for the CHEMKIN calculations. The measured and calculated OH profiles are in excellent agreement over the most of the measured domain for all flames studied. Since the calculated OH profile is very sensitive to the input temperature profile, this agreement gives us confidence in the accuracy of the measured temperatures.

Comparing the measured maximum temperature ($T_{\text{max}}$) with the adiabatic flame temperature for each mixture ($T_{\text{ad}}$), both given in Table 4.1, shows substantial heat loss to the burner, with the flames with lowest flow rate being
nearly 400 K cooler than the adiabatic free flames. As observed in Figure 4.1, $T_{\text{max}}$ increases with increasing flow rate (decreasing stabilization) for all mixtures. Based on earlier observations [6-8], we expect this decrease in stabilization to be reflected in the NO mole fraction, as will be seen below. We note in Table 4.1 that $T_{\text{max}}$ increases steadily with increasing equivalence ratio. This has observed previously by Berg et al. [3], and based on CHEMKIN calculations solving the energy equation we ascribe this behavior partly to the fact that the richer flames are closer to equilibrium immediately downstream of the flame front than leaner flames [3]. Further, since the mass flux for the richer flames is closer to the free flame value, the flame temperatures are closer to the adiabatic values [6].

4.3.2 CH and NO profiles

The measured profiles of the CH and NO mole fractions are shown in Figures 4.2 and 4.3 for Flames A-D. Besides a slight shift in the position of the CH maximum towards the burner surface and narrowing of the CH profile with increasing flow rate, the Figures show that the maximum CH mole fraction ($X_{\text{CH\max}}$) increases by nearly a factor of 2 between 3 and 5 l/min for all equivalence ratios. The measured $X_{\text{CH\max}}$ and mole fraction of NO at 1.6 cm ($X_{\text{NO,1.6}}$) are also given in Table 4.1. The NO mole fraction at 1.6 cm increases monotonically with increasing flow rate. Comparison of the measured and predicted CH profiles obtained from GRI-Mech 3.0 show near quantitative agreement for both CH and NO for all Flames A and B at $\phi = 1.3$ (Figure 4.2), while the differences with the model increase with equivalence ratio. The model calculations show that the slow growth in the post-flame zone is primarily from the Zeldovich mechanism in Flames A and B, while the Zeldovich contribution is negligible in Flames C and D, and that the slow growth in these flames is due to the oxidation of HCN. It will be useful for the discussion to consider the expected amount of Fenimore NO using equation (1.11) and the experimental CH and temperature profiles, while the other quantities are taken from CHEMKIN calculations. The results of the integration up to 1.6 cm axial distance ($X_{\text{NO,Fen}}$) are also given in Table 4.1. Here, due to the experimental uncertainties, we must consider the resultant integration as $\sim 30\%$ accurate. This uncertainty notwithstanding, the agreement between $X_{\text{NO,Fen}}$ calculated with equation (1.11) at 1.6 cm and the measured NO
at the same location is within 10% for all Flames A-C. This degree of internal consistency lends support for the current choice for the rate of the CH+N\(_2\) reaction. The excellent agreement between the GRI-Mech 3.0 calculations and the measurements for flames A and B in Figure 4.2, which trivially yields agreement between the predicted NO (deducting the Zeldovich component) and the integrated rate using the calculated CH profile in equation (1.11), suggests better accuracy for the experimentally derived \(X_{NO,Fen}\) than that inferred from the uncertainty in the measurements. Regarding the recent discussion of the primary product of the CH+N\(_2\) reaction [9,10], we point out that whether the products are HCN+N or NCN+H, 2 atoms of nitrogen are fixed in the process, which ultimately become NO. Regardless of the direct products, the rate of this reaction must be the same as that used here to reproduce the NO measurements [11].
Figure 4.2 Measured and calculated of CH and NO mole fractions for flames A1-A3 and B1-B3. Filled circles denote CH, open diamonds, NO. Lines denote calculated results: solid lines are CH, dashed lines are NO.
Figure 4.3 Measured and calculated of CH and NO mole fractions for flames C1-C3 and D1-D3. Filled circles denote CH, open diamonds, NO. Lines denote calculated results: solid lines are CH, dashed lines are NO.
4.3.3 Effects of burner stabilization

We first consider the origins of the decrease in NO mole fraction with increasing stabilization. The agreement of the $X_{NO,Fen}$ with the measured NO for Flames A-C shown in Table 4.1 permits an examination of the contributing factors in equation (1.11). First, we estimate the change in the factor $k_{f4}(T(x))/T(x)$ at the peak of the CH profile. The temperature at this axial distance is ~100 K lower at 3 l/min than at 5 l/min for all equivalence ratios, which lowers $k_{f4}(T)/T$ in equation (1.11) by ~25%. However, the largest contribution to the decrease in NO mole fraction in equation (1.11) is the decrease in the area of the CH profile by nearly a factor of two between 5 and 3 l/min for each equivalence ratio (reflected by the changes in $X_{CH_{max}}$). Although there appears to be some degree of uncertainty as to the dominant routes forming CH [12], the major reactions all require flame radicals, which, as reflected by the OH data in Figure 4.1, decrease substantially with increasing stabilization. Nevertheless, as shown in Table 4.1, the actual decrease in NO mole fraction with stabilization is ~40% in all cases, rather than the factor of two suggested by the decrease in CH. An important mitigating factor in considering the quantitative interpretation of the changes in CH with stabilization is the change in residence time, reflected in $1/\rho v$ in equation (1.11), which decreases by 5/3 between the highest and lowest flow rates.

4.3.4 Variation in equivalence ratio

Continuing the discussion above, we see that in Table 4.1, in contrast to results for Flames A-C, the Fenimore contribution for D1-D3 ($\phi = 1.5$) is now more than 30% higher than the measured NO. Although just at the limits of the uncertainty of the estimates, we take this observation as reflecting retardation in the rate of conversion of fixed-nitrogen species to NO. No matter which species are the direct products of CH+N$_2$, stable species such as HCN remain important intermediates en route to NO, and conversion to NO could be substantially delayed due to the lack of (oxygenated) radicals under these fuel-rich conditions. We observe a gradual but progressive increase in the experimental NO profiles in the D Flames downstream of the CH profiles.
(Figure 4.3), even though Zeldovich formation is negligible, which is consistent with slow HCN oxidation. Indirect evidence of residual fixed nitrogen species in burner-stabilized flames has been observed [13] at atmospheric pressure and was ascribed to HCN. The calculations using GRI-Mech (see below) show substantial quantities of HCN at 1.6 cm for this equivalence ratio, which is responsible for the increase in the calculated NO profile in Figure 4.3. We also note in Table 4.1 a modest general increase in measured NO mole fraction with increasing equivalence ratio. The origins of both the increase in Fenimore NO and this general trend can be illustrated by comparing Flames B2 and D2, shown in Figure 4.4; here, for convenience the profiles have been shifted so that the maxima of the CH profiles coincide. Increasing the equivalence ratio from 1.3 to 1.5 at 4 l/min increases the measured NO mole fraction at 1.6 cm by ~30%, while $X_{NO,Fen}$ increases by 60% (see Table 4.1). The fact that these flames have the same maximum CH mole fractions facilitates their comparison in terms of the integrated rate in equation (1.11). Comparison of the CH and (fit) temperature profiles in Fig. 4.4 for the two flames shows systematically higher temperatures (~140 K at the maximum of the CH profile) and a wider CH profile (longer trailing edge) in the D2 flame than in B2. In the context of equation (1.11), the higher temperature at the maximum of the CH profile increases the nitrogen fixation rate by ~40%, through $k_{f4}(T)/T$, while the wider CH profile for D2 accounts for the rest of the difference in $X_{NO,Fen}$. In short, even though the two flames have the same maximum CH mole fraction, the higher temperature and wider profile in the richer flame results in higher net NO formation.
Figure 4.4. Experimental CH (points) and fit temperature (lines) profiles for Flames B2 (open circles, dashed line) and D2 (closed circles, solid line). The data for Flame B2 have been shifted such that the maximum of the CH profile coincides with that of that for Flame B2.

4.3.5 Comparison with model predictions

As mentioned above, the GRI-Mech 3.0 predictions for CH and NO are in near quantitative agreement with the measurements in all flames A and B, and become progressively worse with increasing equivalence ratio (see Figures 4.2 and 4.3). The discrepancies in the peak CH mole fractions are at the limits of the uncertainty, but the differences in width of the CH profile and the magnitudes of NO mole fractions are outside the measurement uncertainty. The agreement at $\phi = 1.3$, and the consistency of the measured NO and $X_{NO,Fen}$ suggest that the increasing discrepancy in the predicted NO profiles be sought in the disagreement in the CH profiles [12].

The agreement between measured NO and $X_{NO,Fen}$ for the C Flames is within 10% and if the computed CH profile could be fixed to the experimental profile, the NO profiles would also agree, since all computed NO arises from the Fenimore mechanism with almost no ($<5$ ppm) HCN at 1.6 cm. However, preserving the agreement in the CH profiles at $\phi = 1.3$ (and other equivalence ratios) is an important precondition when considering changing mechanisms. Whereas adjusting the predicted CH profile in the D Flames would bring the Fenimore contribution into better agreement with that experimentally derived, the assessment of the adequacy of the resulting prediction is frustrated by the
lack of direct evidence for “residual” HCN, which is necessary to assess the prediction of the total fixed nitrogen. In this regard, the detailed calculations predict 25 ppm HCN at 1.6 cm in Flame D1, decreasing to only a few ppm in D3 caused by the increase in temperature (more rapid oxidation) with decreased stabilization. Another complication is that the model calculations for the D flames predict significant (> 10%) NO formation via C+N2, which if true limits the validity of using equation (1.11) to estimate the total NO formed in these flames.

4.4 Summary and Conclusions

At equivalence ratios between 1.3 and 1.5, increasing burner stabilization by decreasing the flow rate from 5 l/min to 3 l/min lowered the maximum CH mole fraction by a factor of two, and the NO mole fraction by ~40% in all flames studied. Integrating the rate for CH+N2 to estimate Fenimore NO formation, using the rate coefficient in GRI-Mech 3.0, and the measured temperatures and CH profiles, shows very good agreement with the measured NO mole fraction for $\phi = 1.3$ and 1.4, and supports the current choice for this rate. The increase in residence time caused by increased stabilization is also seen to be an important factor when considering the impact of the changes in CH mole fraction on NO formation. The results at $\phi = 1.5$ suggest that substantial quantities of fixed nitrogen species, e.g. HCN, are only slowly oxidized in the post-flame zone under these conditions. Detailed calculations using GRI-Mech 3.0 predict the experimental results at $\phi = 1.3$ nearly quantitatively, but show increasing differences with the measurements for both CH and NO profiles with increasing equivalence ratio. While some of these differences may be addressed by improving the CH prediction, the analysis indicates that the fate of species such as HCN and the contribution from other nitrogen-fixing species, such as the C atom, must also be investigated at $\phi = 1.5$ and higher.
Bibliography


