

Influence of Thermochemistry on Prompt NO formation in Flames

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Abstract

In this work, with the exception of NCN, the influence of thermochemistry on prompt NO formation in flames is studied for the first time. Since prompt NO formation is more pronounced under rich conditions, we investigated two fuel-rich methane and acetylene flames. To estimate the sensitivity of the species, we formulated a sensitivity equation based on the maximum NO concentration. We varied the enthalpy of formation of the species by ± 1 kJ and ± 5 kJ to perform the sensitivity analysis. Our analysis shows that the prompt NO formation is mainly affected by the thermochemistry of NCN, CH, N₂, and H species.

1. Introduction

NO is one of the major pollutants from combustion processes. Formation of NO occurs, dependent on the flame conditions, *via* different reaction pathways e.g. thermal NO, prompt NO, fuel NO, NNH, and N₂O mechanisms. The thermal NO pathway is the most important source of NO under high temperature combustion ($T > 1800$ K) [1]. In this pathway, O-radicals attack the triple bond of N₂ forming NO and N. The prompt NO formation pathway is initiated by the rapid reaction between CH_{*i*} radicals and N₂ [2]. For low temperature combustion devices, this pathway is the most important source of NO in turbulent hydrocarbon-air diffusion flames [3]. The other pathways of NO formation involving NNH [4] or N₂O [5] are more complex and not yet fully understood.

Fenimore [6] identified the reaction of CH_{*i*} radicals with N₂ as the most important initial step for the formation of prompt NO. He postulated that $\text{CH} + \text{N}_2 \rightleftharpoons \text{HCN} + \text{N}$ as primary initiation step for the “prompt” NO pathway. This postulate remained unchanged until Moskaleva and Lin (2000) [7] showed by an *ab initio*/statistical rate theory study that the insertion of CH into the triple bond of N₂ is more

likely to lead to NCN and H. Recent theoretical [8,9] and experimental [10,11] studies have confirmed the formation of NCN from the reaction of CH and N₂, which eventually leads to the formation of NO at high enough temperatures. With this, the oxidation reactions of NCN with O₂, O, H, and OH constitute an important part of the nitrogen chemistry in flames. These chemical pathways, together with the established NO formation pathways remarkably capture the experimental trends [10–13]. NCN is a key species whose thermodynamic properties, namely the Gibbs free enthalpy G , largely influence the partial equilibrium of the $\text{CH} + \text{N}_2 \rightleftharpoons \text{NCN} + \text{H}$ reaction, and thereby the prompt NO formation [8,14].

In recent years, the thermochemistry of NCN has gained significant attention in the combustion community. The reported values for the enthalpy of formation ($\Delta_f H^0_{298}$) of NCN differ significantly (± 10 kJ/mol). This discrepancy largely impacts the modeling of NO formation in flames. In 2013, Goos et al. [15] comprehensively reviewed and critically analyzed the available data for the NCN enthalpy of formation [8,16–18]. The authors [15] reported a value of 457.8 ± 2 kJ/mol for $\Delta_f H^0_{298}$ of NCN. Their value excellently matches with the theoretical values by Harding et al. [8] (458.76 kJ/mol) and Teng et al. [9] ($\Delta_f H^0_{298} = 457.73$ kJ/mol). However, Lamoureux et al. [19] proposed a lower value ($\Delta_f H^0_{298} = 444.3$ kJ/mol) in their modeling work to achieve a satisfactory agreement between their measurements and calculation in their work for flame structure analysis. In 2018, Klippenstein et al. [2] and Harding and Olzmann [20] theoretically obtained 450.80 ± 0.68 kJ/mol and 452.2 ± 1.0 kJ/mol, respectively, for the values of $\Delta_f H^0_{298}$ of NCN. Both values agree excellently with the highly accurate ATcT database ($\Delta_f H^0_{298} = 450.42 \pm 0.64$ kJ/mol) within the stated uncertainty.

Despite great scientific efforts, accurate modeling of NO formation in flames remains a challenging task. Most published studies have focused on methane flames. Flames with higher hydrocarbon fuels have received less attention. Beside the thermochemistry of NCN, none of the studies investigated the influence of the uncertainty in the thermochemistry of other species on NO formation in flames. For this reason, the role of thermochemistry on prompt NO formation in flames is investigated in this work.

2. Kinetic Model and Analysis Method

This work adopts the kinetic mechanism from our previous work [21]. The mechanism consists of 125 species and 1121 reversible reactions. Our kinetic model satisfactorily captures the oxidation kinetics of C₁ - C₂ hydrocarbon/oxygenated - NO_x chemistry interaction. Additionally, our model also captures NO species profiles in C₁ - C₂ premixed flames.

In the following, we briefly outline our research methodology to calculate brute force sensitivity coefficients. First, we calculated the respective flames without altering the thermochemistry to obtain a reference mole fraction profile for NO, which is the target property in this work. Second, we altered the enthalpy of formation for each species in the mechanism sequentially for all four test cases reported in this abstract. Finally, we employed equation (1) to calculate the sensitivity coefficient ($S_{i,j}$) for the enthalpy of formation of i_{th} species against the target species j .

$$\text{Sensitivity } (S_{i,j}) = \alpha \left(\frac{x_{\text{max},i,j} - x_{\text{max},\text{ref},j}}{x_{\text{max},\text{ref},j}} \right) \quad (\text{eq. 1})$$

where $x_{\text{max},\text{ref},j}$: maximum mole fraction of target species without any change in thermochemistry; $x_{\text{max},i,j}$: maximum mole fraction of target species (j) when the enthalpy of the i_{th} species is changed; α : is constant given by $\frac{LHV_{\text{fuel}}}{R \times \delta h}$. We used the lower heating value LHV of the fuel to normalize the change in specific enthalpy δh of the investigated species. Sensitivity coefficients were calculated with δh equal to -5, -1, 1 and 5 kJ/mol to investigate the influence of curvature on the sensitivity coefficients.

3 Results and Discussion

To the best of our knowledge, this is the first study investigating the influence of thermochemistry of various species including NCN on the prompt NO formation in flames. All simulations were performed using the LOGEresearch v1.10 [22]. For the burner-stabilized flame modeling, a mixture averaged transport model, thermal diffusion, and radiative heat transfer were considered. The concentrations of all stable species on the burner surface from the gas composition in the feed were computed in addition to the species diffusion close to the boundary. For all the major radicals, their recombination reactions at the burner surface were considered. We used the experimental temperature profile in this work, we will also investigate the impact of the calculated temperature profile.

3.1 Methane Flame

For methane as fuel, we choose a low-pressure burner stabilized flame under fuel-rich conditions ($\phi=1.25$). The flame fueled with $\text{CH}_4/\text{O}_2/\text{N}_2$ was studied experimentally by Lamoureux et al. [19]. We chose a fuel-rich flames because prompt NO formation is favored under rich conditions [21]. Figure 1 shows the normalized sensitivity calculated using eq. 1. A positive sensitivity coefficient means that an increase in species enthalpy of formation will increase the NO concentration and vice versa. As seen, NCN and N_2 show the highest sensitivity followed by H, CH, and CH_3 . This support that the change in the Gibbs free energy ΔG_R of reaction $\text{CH}+\text{N}_2\rightleftharpoons\text{NCN} + \text{H}$, is decisive for the NO formation. Products show a positive, reactants show a negative sensitivity coefficient. Since the uncertainty in the enthalpy of formation of NCN is the highest, it was correct that the thermochemistry of NCN was investigated in prior studies. The thermochemistry of CH_3 , CH, H_2 , H and O is important for CH formation. The similar results in all four calculated sensitivity coefficients for each enthalpy of formation shows that our results are independent on the curvature in the sensitivity coefficients.

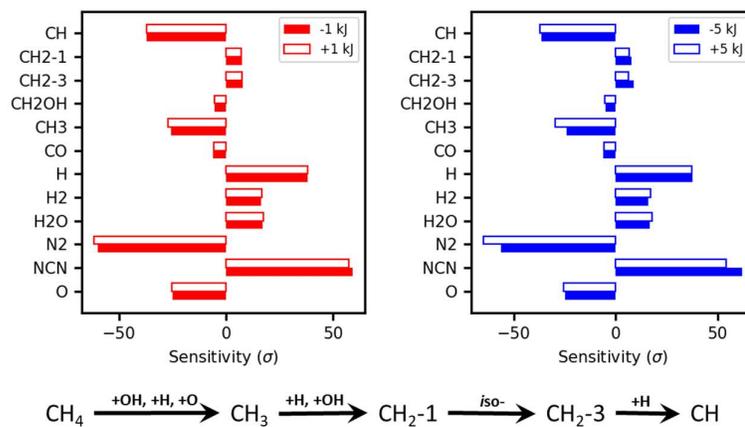


Figure 1: Normalized sensitivity of various species towards NO (upper figure) and CH formation pathway (lower figure) in $\text{CH}_4/\text{O}_2/\text{N}_2$ low-pressure (5.3 kPa) burner stabilized premixed flame at $\phi=1.25$. *iso-*: isomerization.

To further investigate the accuracy in the calculated sensitivity coefficients we show absolute changes in the maximum NO concentration in Fig. 2. The experimental data together with its uncertainty is also shown as solid black line and dashed green lines. It is seen that the uncertainty in the experiments is larger than the uncertainty resulting from the estimation for the enthalpy of formation.

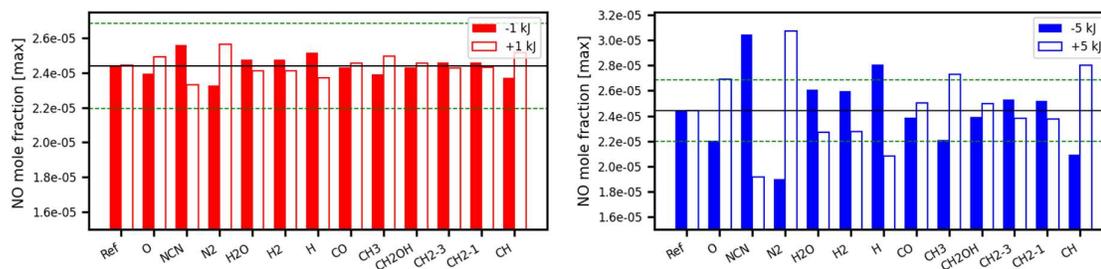


Figure 2: Maximum predicted NO mole fraction obtained by varying the enthalpy of formation of species for low pressure (5.3 kPa), rich ($\phi=1.25$) $\text{CH}_4/\text{O}_2/\text{N}_2$ burner stabilized premixed flame. Horizontal lines: solid black (measured maximum experimental NO mole fraction of [19]), dashed green (upper and lower uncertainty bound quoted in the experiment). Ref: a reference modeling prediction without any changes in thermochemistry.

3.2 Acetylene Flame

Figure 3 illustrates the normalized sensitivity coefficients of various species towards NO in the low-pressure premixed $\text{C}_2\text{H}_2/\text{O}_2/\text{N}_2$ burner stabilized flame. Again, the $\text{C}_2\text{H}_2/\text{O}_2/\text{N}_2$ flame was experimentally studied by Lamoureux et al [19]. As in the methane flame, the topmost sensitive species influencing the NO formation are NCN, CH, N_2 , and H (cf. Fig. 1 and Fig. 3). Again ΔG_R of reaction $\text{CH} + \text{N}_2 \rightleftharpoons \text{NCN} + \text{H}$, is decisive for the thermochemistry. Flow analysis reveals that CH_2-1 is formed *via* HCCO while in methane, it is formed *via* the CH_3 radical. Interestingly, HCCO does not appear as a sensitive species while CH_3 does (cf. Fig. 1 and Fig. 3).

As seen, a variation of the enthalpy by ± 1 kJ did not have much impact on the predicted value of NO mole fraction. The model underpredicts the maximum NO mole fraction for both cases (variation of enthalpy of species by ± 1 kJ and ± 5 kJ). However, one can observe that the decreased enthalpy of NCN and H, and the increased enthalpy of N_2 and CH by 5 kJ have caused a large positive impact on the predicted mole fraction of NO (see Fig. 4(right)). This is further illustrated in Fig. 5.

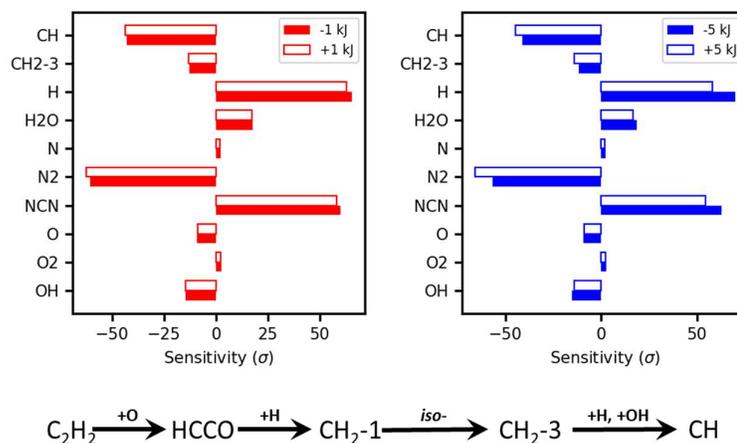


Figure 3: Normalized sensitivity of various species towards NO (upper figure) and CH formation pathway (lower figure) in $\text{C}_2\text{H}_2/\text{O}_2/\text{N}_2$ low-pressure premixed flame at $\phi=1.25$. *iso-*: isomerization.

In contrary to the methane flame, where the model predictions agree remarkably with the experiments, NO predictions are not accurate enough for C_2H_2 premixed flame even with ± 5 kJ change in enthalpy of the species. In literature, NCN heat of formation is still within the discrepancies of ± 10 kJ. The thermochemistry of other species (e.g. N_2 , H) except NCN are well established (uncertainty of ± 1 kJ).

Therefore, we conclude that, beside NCN thermochemistry, the observed discrepancy for prompt NO formation is very likely in the oxidation kinetics of C_2 flames.

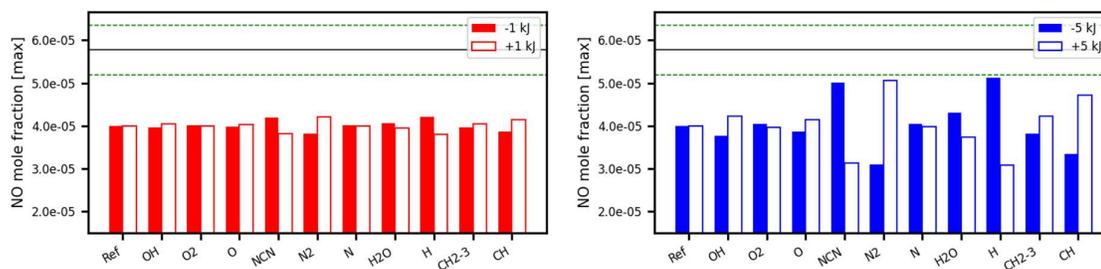


Figure 4: Predicted maximum NO mole fraction by varying the enthalpy of species in low pressure (5.3 kPa), rich ($\phi=1.25$) $C_2H_2/O_2/N_2$ premixed flame. Horizontal lines: solid black (measured maximum experimental NO mole fraction of [19]), dashed green (upper and lower uncertainty bound quoted in the experiment). Ref: a reference modeling prediction without any changes in thermochemistry.

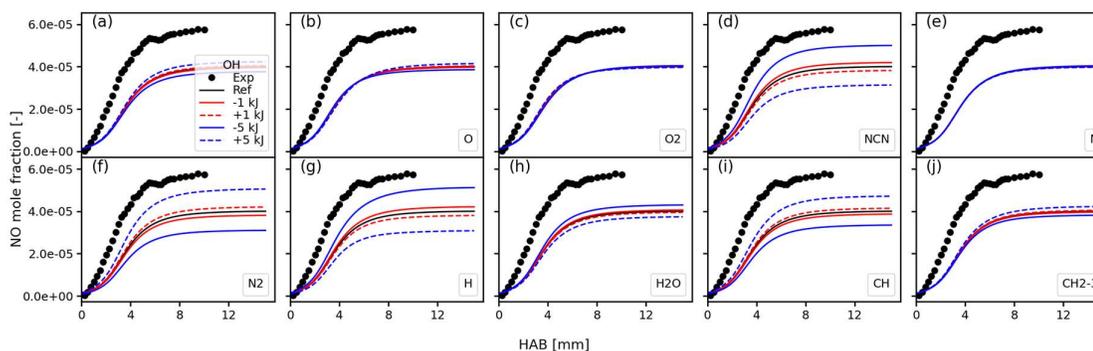


Figure 5: Comparison between the experimental and modeled NO profiles as a function of height above the burner for the low pressure (5.3 kPa), rich ($\phi=1.25$) $C_2H_2/O_2/N_2$ premixed flame. For simulation, the enthalpy of species is varied as indicated in the figure legend. Symbols: experimental data [19], Ref: a reference modeling prediction without any changes in thermochemistry.

4 Conclusion

We assessed the sensitivity of the thermochemistry of various species in the predictions of prompt NO formation in methane and acetylene flames under rich conditions. For the analysis, we changed the enthalpy of all species in the mechanism by ± 1 kJ and ± 5 kJ. We found that NCN, H, N_2 , and CH are the most sensitive species influencing NO prompt formation. This shows that ΔG_R of reaction $CH+N_2 \rightleftharpoons NCN + H$, is decisive for the thermochemistry of NO formation. In addition, most of the radical species were found to be sensitive. In acetylene flame, the modeling results are still not agreeing within the experimental uncertainty even after varying the enthalpy of species by ± 5 kJ. Therefore, we conclude that, beside NCN thermochemistry, the insufficiency of the model to accurately predict NO in acetylene flames may lie in the oxidation kinetics. Further investigations are needed to study: 1) Impact of calculated temperature profile 2) Impact of experimental temperature profile uncertainty and 3) Combination of thermodynamic uncertainty and rate constant uncertainty.

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