

Prompt NO formation in flames: The influence of NCN thermochemistry

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Abstract

The influence of the route via the NCN radical on NO formation in flames was examined from a thermochemistry and reaction kinetics perspective. A detailed analysis of available experimental and theoretical thermochemical data combined with an Active Thermochemical Tables analysis suggests a heat of formation of 457.8 ± 2.0 kJ/mol for NCN, consistent with carefully executed theoretical work of Harding et al. (2008) [5]. This value is significantly different from other previously reported experimental and theoretical values. A combination of an extensively validated comprehensive hydrocarbon oxidation model extended by the GDFkin3.0_NCN-NO_x sub-mechanism reproduced NCN and NO mole fraction profiles in a recently characterized fuel-rich methane flame only when heat of formation values in the range of 445–453 kJ/mol are applied. Sensitivity analysis revealed that the sensitivities of contributing steps to NO and NCN formation are strongly dependent on the absolute value of the heat of formation of NCN being used. In all flames under study the applied NCN thermochemistry highly influences simulated NO and NCN mole fractions. The results of this work illustrate the thermochemistry constraints in the context of NCN chemistry which have to be taken into account for improving model predictions of NO concentrations in flames.

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1. Introduction

Prompt NO formation is a fascinating topic in combustion chemistry since the first report of the phenomenon by Fenimore [1] more than thirty years ago. The issue remained controversial until

now. Fenimore attributed the residual NO observed close to burner surface in hydrocarbon flames to reactions involving molecular nitrogen and free radicals of hydrocarbons. He suggested the reactions



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as potential sources of NO formation.

Later an examination of prompt NO formation by Miller and Bowman [2] concluded that reaction (R1a) is responsible for the phenomenon.

However, studies of Cui et al. [3] and Moskalva and Lin [4] changed the picture by showing that (a) the spin–orbit coupling in reaction R1a was not strong enough to account for experimental observations regarding prompt NO formation and that (b) the alternative product channel



may better account for the experimental results reported at that time. These findings sparked many consecutive studies providing evidence for the suggested new route. A central issue emerged—from experimental, theoretical and modeling perspectives—namely the value of the rate coefficient of R1b in the practically important temperature range around 1500 K. The extensive theoretical study on R1b by Harding et al. [5] agreed quantitatively with the shock tube study of Hanson and co-workers [6]. This finding clearly suggested that a central aspect of NCN reaction kinetics is settled. However, in their paper Harding et al. [5] pointed out that more accurate measurements of the heat of formation of NCN would significantly reduce the remaining uncertainty of their theoretical predictions below 2000 K. Considering the endothermicity of R1b it is obvious that the heat of formation for NCN is likewise a highly sensitive quantity for modeling predictions, when the NCN pathway for prompt NO formation is implemented in reaction mechanisms. However, the relevance and extent of this uncertainty has not been systematically addressed [7–9]. So far reported values for the heat of formation of NCN differ by ~ 20 kJ/mol [10–12].

El Bakali et al. [7] suggested, based on NCN measurements in flames, using a rate coefficient significantly faster than Moskalva and Lin's value [4] but different from Harding et al. [5] and Vasudevan et al. [6]. In the more recent study of Lamoureux et al. [13] on CH, NCN and NO formation in fuel-rich methane and acetylene flames, the kinetic data of Hanson and co-workers for reaction (R1b) was used for kinetic modeling. The agreement of model predictions and experiment in this recent work also suggest a consistent picture regarding the modeling of prompt NO formation in methane flames.

However, all previous modeling studies on NO and NCN formation relied on kinetic models tested mainly for methane flames and much less for other fuels and other reactor types [7–9]. As a consequence the examination of a different fuel, e.g. acetylene in addition to methane, can imply using a different kinetic scheme [13] which is an unsatisfactory situation. Therefore it is highly desirable that up to date NO_x sub-mechanisms

including NCN chemistry are implemented into general hydrocarbon oxidation models, which map the complete set of combustion features (ignition delay times, flame speeds, speciation in reactors and flames, engine modeling) and fuels (C1–C4 hydrocarbons, *n*-heptane, toluene, etc.).

This point leads to the main objectives of the present work. First, the quality of available thermochemical data of NCN will be critically analyzed accompanied by quantum chemical calculations using state of the art techniques. Second, a general hydrocarbon oxidation mechanism will be extended for simulating NO formation via the NCN pathway. Based on the analysis of NCN thermochemistry and using a comprehensive kinetic model the effect of different scenarios for the absolute value of the heat of formation of NCN in model predictions regarding NO formation in hydrocarbon flames will be tested and implications for modeling NO and NCN formation will be discussed.

2. Methods

2.1. Thermochemistry

In order to use a consistent set of thermochemical data for kinetic modeling, enthalpies of formation obtained with the Active Thermochemical Tables (ATcT) [14,15] approach were employed whenever possible and used to update the Goos et al. thermochemical database [16]. The ATcT enthalpies of formation utilized the most current version [17] of the underlying Thermochemical Network (TN), which was recently engaged to produce new thermochemistry data for phenyl and halobenzenes [18], bromine oxides [19] and small hydrocarbon radicals [20].

In addition, the enthalpy of formation of NCN (CAS-number: 2669-76-3) was examined in detail and re-evaluated using ATcT, and NCN heat capacity, entropy, and enthalpy increment; and the corresponding polynomials [21,22] were recalculated within the rigid-rotor-harmonic-oscillator (RRHO) approximation using the PAC program of McBride and Gordon [23], based on spectroscopic data listed in Jacox [24].

2.2. Kinetic model

The hydrocarbon oxidation model is the current version of a C1–C4 fuel base-mechanism first reported in [25]. The compilation strategy aims at continuously increasing the number and type of targets for mechanism validation. Important extensions were the inclusion of *n*-heptane oxidation at high and low temperatures [26], a methanol oxidation sub-mechanism developed by Dryer group (see [27] and literature cited therein) and the oxidation of toluene as reported in [28]. In

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