The Reaction NCN + H₂: Rate constant measurements, theoretical modeling, and influence on prompt-NO formation

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Nitrogen oxides (NOₓ) are undesired combustion byproducts that cause damage to the environment. To develop NOₓ reduction strategies, a detailed understanding of the underlying chemical mechanisms, in particular of the prompt-NO formation pathway that gains importance in low temperature combustion, is important.

In contrast to the traditional Fenimore mechanism, it has been shown that NCN (instead of HCN) is the main product of the prompt-NO initiation reaction \( \text{CH} + \text{N}_2 \rightarrow \text{NCN} + \text{H} \). Although the implementation of NCN radical reactions improves modeling of NOₓ formation, many common flame mechanisms still do not account for NCN chemistry. In recent years, in order to develop reliable NCN submechanisms, we have used the shock tube method to directly measure rate constants of NCN reactions and performed quantitative flame studies aiming at the detection of relevant flame intermediates and the validation of the submechanism performance.

This study is concerned with a thorough analysis of the role of the so far neglected reaction NCN + H₂. Recently, we have provided first direct rate constant measurements and, assuming HNCN + H as the sole products, implemented this reaction into the detailed GDFkin3.0_NCN mechanism together with a set of reactions for subsequent HNCN and HNC chemistry [Faßheber, Lamoureux, Friedrichs, Phys. Chem. Chem. Phys. 17 (2015) 15876]. A new NCN → HNCN → HNC → HNCO → NH₂ → NH → NO pathway had been identified. Here, we present high-level theoretical calculations aiming both at the clarification of the product branching ratio and of the total rate constant. HNCN could be confirmed as the main product, however, some disagreement was found between experimental and theoretical data with respect to the temperature dependence of the total rate constant. These could be traced back to additional fast reactions of the electronically excited \(^1\text{NCN}\) radical, which is initially formed in the thermal decomposition of cyanogen azide (NCN₃), which was used as the NCN precursor in the shock tube experiments. Consequently, the distinctively different \(^1\text{NCN}\) radical reactions have been investigated theoretically as well and, based on the predicted \(^1\text{NCN} + \text{H}_2\) rate constants, the original shock tube data have been reanalyzed. Compared to the previously recommended values, the rate constant of the reaction \(^3\text{NCN} + \text{H}_2\) turns out to be a factor of 5 lower at \( T = 1000 \, \text{K} \), however, at a more typical combustion temperature of \( T = 1750 \, \text{K} \), the updated result remains in accordance with previous work.