

Shock-Tube Study of the Thermal Decomposition of NCN

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Abstract

The decomposition of NCN was studied behind reflected shock waves in the temperature range 1800–2800 K at pressures near 1 bar. Highly diluted mixtures of NCN_3 in argon were shock-heated to produce NCN, and concentration-time profiles of C and N atoms were monitored by C- and N-ARAS (atomic resonance absorption spectroscopy) at 156.1 and 119.9 nm, respectively. There are two possible NCN decomposition channels leading to $\text{C} + \text{N}_2$ or $\text{N} + \text{CN}$. Our experiments indicate that the $\text{C} + \text{N}_2$ channel is the dominant pathway, which confirms results of an earlier theoretical study by Moskaleva and Lin. For this channel the temperature dependence of the rate coefficient was determined.

Introduction

The emission of NO and NO_2 (NO_x) from combustion processes is of general environmental concern. Nitrogen oxides are of crucial importance in the production of tropospheric ozone and secondary pollutants like peroxyacetyl nitrates, they contribute to the acidification of rain and participate in the destruction of stratospheric ozone. To minimize the emission of NO_x , a better understanding of the formation mechanisms and their kinetics is needed.

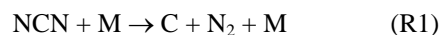
There are two major pathways of NO_x formation in hydrocarbon combustion: The thermal or Zeldovich mechanism [1] and the prompt or Fenimore mechanism [2]. Under fuel-lean conditions the thermal formation mechanism is most important. It is initialized by the reaction $\text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N}$, and the overall kinetics is well known. But under fuel-rich conditions, NO formation via the Fenimore mechanism can also play a role. Under which conditions the latter mechanism may contribute to NO_x formation under fuel-lean conditions is a subject of discussion [3], also because kinetic data for this mechanism are scarce and uncertain. The initial steps are probably reactions of small hydrocarbon radicals with N_2 , where the $\text{CH} + \text{N}_2$ reaction is considered to be of crucial importance.

For a long time it was believed that the products of $\text{CH} + \text{N}_2$ are mainly $\text{HCN} + \text{N}$, formed in a spin-forbidden reaction [2]. But all theoretical calculations of the rate coefficient of $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$ led to much smaller values than experimentally observed. In the year 2000 Moskaleva and Lin [4] published a quantum chemical study of the spin-allowed reaction $\text{CH} + \text{N}_2 \rightarrow \text{NCN} + \text{H}$ and suggested this reaction to be the principal pathway. Subsequently, NCN has been detected in low-pressure hydrocarbon flames by Smith [5], Sutton *et al.* [6], Lamoureux *et al.* [7], and Klein-Douwel *et al.* [8]. A shock-tube study of Vasudevan *et al.* [9] also confirmed that NCN and H are the major products. Furthermore, there is a very recent theoretical study of Harding *et al.* [10], in which multireference *ab initio* methods and transition-state theory was used to characterize the $\text{CH} + \text{N}_2$ reaction. All these studies point out that NCN is an important intermediate in the

formation mechanism of prompt NO. Accordingly, Elbakali *et al.* [11] and Sutton and Fleming [12] changed the $\text{HCN} + \text{N}$ to the $\text{NCN} + \text{H}$ channel in complex combustion mechanisms (GDF-Kin 3.0, GRI 3.0) and compared simulation results of the modified and the original mechanism with experimental results.

Unfortunately, only few data on the kinetics of NCN reactions are available. It could possibly react with H, O, OH or O_2 to directly form NO or other reactive species (CN, HCN, NH, and NCO), which can be further oxidized and finally also produce NO. There are two theoretical studies by Zhu and Lin on $\text{NCN} + \text{O}_2$ [13] and $\text{NCN} + \text{O}$ [14], one study by Vasudevan *et al.* [9], where the rate coefficient of the $\text{NCN} + \text{H}$ reaction is inferred from a shock-tube study of the $\text{CH} + \text{N}_2$ reaction, and several studies on the reaction $\text{NCN} + \text{NO}$ [15–19].

Only one theoretical study by Moskaleva and Lin [20] deals with the thermal decomposition of NCN. These authors performed high-level quantum chemical calculations on the $\text{C} + \text{N}_2 \leftrightarrow \text{N} + \text{CN}$ reaction, which was shown to proceed through CNN, NCN, and cyclic *c*-NCN intermediates. On the basis of the calculated molecular parameters and the potential energy surface, rate coefficients were obtained from multichannel variational RRKM theory. In general, the decomposition of NCN can proceed via the following two product channels:



Moskaleva and Lin reported temperature dependences of the unimolecular rate coefficients for both reactions in the range $T = 700\text{--}4500$ K and pressures of 1 Torr, 100 Torr, and 1 atm. Their rate coefficient of R1 is one or two orders of magnitude larger than that of R2.

In the present work, we report on the first experimental study of the thermal decomposition of NCN. By time-dependent detection of C and N atoms with atomic resonance absorption spectroscopy (ARAS), it

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could be confirmed that reaction R1 is the major NCN decomposition channel, and a rate coefficient for R1 was determined.

Experimental

Shock Tube. All experiments were carried out behind reflected shock waves in a stainless steel shock tube with an inner diameter of 10 cm. The shock tube is divided in a 3.05 m long high-pressure part and a 4.20 m long low-pressure part by an aluminum foil. For the optical detection, there are two MgF₂ windows in the low-pressure section. For further details see ref. [21] and the literature cited therein. Before each experiment, the whole shock tube was evacuated to pressures of around 10⁻⁶ mbar, and the low-pressure section was filled with the test gas, *i.e.*, NCN₃ highly diluted in Ar (99.9999 %, Air Liquide). Hydrogen (99.9 %, Air Liquide) was used as a driver gas to initiate the shock wave by pressure bursting of the aluminum foil. By varying the initial pressure in the low-pressure section and the thickness of the aluminum foil, different postshock temperatures and pressures can be obtained. To calculate these postshock conditions, the velocity of the incident shock wave was measured with four fast piezo-electric pressure transducers. This velocity together with the initial temperature and pressure was used to calculate the conditions behind the reflected shock wave by using the familiar one-dimensional conservation equations [22].

ARAS measurements. The setup for the ARAS detection basically comprises a microwave-powered discharge lamp, a vacuum UV monochromator (Acton Research Corporation, Spectra Pro VM-504), and a solar-blind photomultiplier tube (Hamamatsu R1259). The discharge lamp consists of a quartz tube, which is flushed by the lamp-gas mixture, and an Evenson cavity connected to a microwave generator. The operating power was always 150 W, and the pressure in the lamp was around 8 mbar.

C atoms were detected at 156.1 nm (2p³ ³D_J^o → 2p³ ³P_J), where we used mixtures of 1% CO in He for the discharge lamp. Because of self-absorption and self-reversal in the lamp and nonresonant emission from the (1,1) vibrational band of CO (A¹Π → X¹Σ⁺) [23], we had to perform calibration experiments to convert the measured absorbances into C-atom concentrations. For this calibration we performed pyrolysis experiments with mixtures of 20 or 30 ppm CH₄ (99.995 %, Messer Griesheim) in Ar. The recorded absorbance-time profiles were compared to simulated C atom concentration-time profiles obtained with an updated version [24] of the mechanism published by Dean and Hanson [25]. We carried out calibration experiments at temperatures between 2630 and 2970 K and pressures of around 1 bar. Since all the obtained calibration curves fell into a narrow range and did not show any discernible systematic temperature dependence, we used an averaged curve to calibrate the results of our NCN decomposition experiments.

N atoms were detected by employing the N I triplet (3s ⁴P_J → 2p ⁴S_{3/2}^o) at 119.9 nm [26]. The lamp mixture contained 1% N₂ and 99% He. For the calibration we used mixtures of 200 to 300 ppm N₂O and ~10% N₂ in Ar. The temperature of the calibration experiments varied between 2160 and 2440 K. For the modelling we used a simple mechanism with 7 reactions [26, 27], where the two most important reactions turned out to be N₂O + M → N₂ + O + M and O + N₂ → NO + N.

Synthesis of NCN₃. Since NCN₃ is very explosive in solid and liquid state, we adopted a synthesis yielding gaseous NCN₃ described by Milligan *et al.* [19, 28]. This procedure uses the reaction of NaN₃ with BrCN and produces NaBr and the desired NCN₃. A mass spectrum of the obtained product shows a residual contamination of BrCN not exceeding 5%.

Results and Discussion

For the shock tube experiments, we prepared mixtures of ~5, ~15 and ~30 ppm NCN₃ in Ar. The measurements were performed behind reflected shock waves in a temperature range from 1800–2800 K. The pressure varied from 1.1 bar at 2800 K to 1.5 bar at 1800 K. Under these conditions, NCN₃ is supposed to decompose very fast to N₂ + NCN.

A typical C atom concentration-time profile is shown in Fig. 1. The rate coefficient for reaction R1, can be obtained from a linear fit of the first-order rate law to the initial slope:

$$k_1 = \frac{1}{[\text{NCN}]_0} \cdot \left(\frac{d[\text{C}]}{dt} \right)_{t \rightarrow 0} \quad (1)$$

Here, the initial concentration [NCN]₀ is assumed to be equal to the initial concentration of cyanogen azide, [NCN₃]₀.

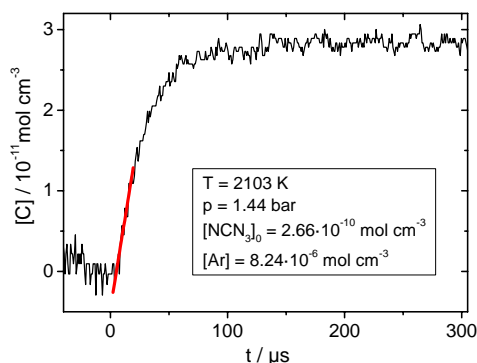


Fig. 1. Experimental C atom concentration-time profile (black line) and linear fit to the initial slope (red line).

The rate coefficients obtained in this way are displayed in Fig. 1. They show a positive temperature dependence, which can be described by the following expression:

$$k_1 = 7.5 \times 10^8 \exp\left(\frac{-25740 \text{ K}}{T}\right) \text{ s}^{-1} \quad (2)$$

An Arrhenius plot of our results along with the prediction of Moskaleva and Lin [20] is shown in Fig. 2. The temperature dependence found in our experiments is a little bit weaker, but the absolute values are in reasonable agreement with the predictions. The uncertainty of our absolute values mainly reflects the uncertainty in the calibration mechanism. Depending on the mechanism used, the results for the rate coefficients differ by about 50%. The calibration mechanism we finally used was the most adequate one in reproducing the complete carbon atom concentration-time profiles in our calibration experiments. In comparison to the calculated values of Moskaleva and Lin, our experimentally determined values are at most a factor of three larger (for the lowest temperatures). We note that in contrast to the absolute values, the temperature dependence is only very little affected by the calibration mechanism.

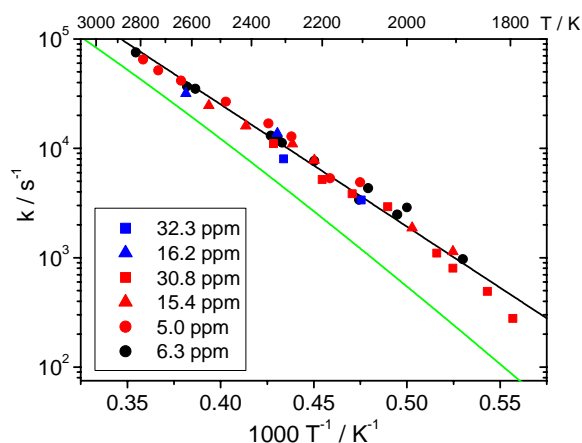


Fig. 2. Temperature dependence of the rate coefficient k_1 for pressures between 1.1 and 1.5 bar; full symbols: experimental values, black line: linear fit (eq. 2), green line: calculation by Moskaleva and Lin for 1013 mbar [20].

Over the whole temperature range, the N-atom concentrations we detected were much lower than the C-atom concentrations. Therefore, the dominating reaction pathway for NCN decomposition is likely to be reaction R1. This is in accord with the predictions of Moskaleva and Lin [20]. Further studies on the pressure dependence and the channel branching are underway in our laboratory.

Conclusions

The thermal decomposition of NCN at elevated temperatures was experimentally studied for the first time. Time-resolved concentration-time profiles for the reaction products C and N were monitored behind reflected shock waves by using atom resonance absorption spectrometry. The reaction leading to C + N₂ was identified as a major reaction pathway, and the temperature dependence of its rate coefficient in the range $T = 1800\text{--}2800$ K was determined at pressures near 1 bar.

Acknowledgements

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