

Multiple Detection Schemes for Investigating High-Temperature Radical Cross Reactions of NCN behind Shock Waves

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Cyanonitrene, NCN, is a key radical in the complex reaction mechanism of prompt-NO formation, which is one of the main pollutant processes in fuel-rich hydrocarbon combustion [1]. The kinetic investigation of NCN reactions at high temperatures, in particular reactions with other transient species, is challenging since suitable precursors and sensitive fast detection schemes are required. In this context, we present shock tube studies of four different reactions measured on the μs time scale. The highly reactive diradical NCN has been made available by thermal decomposition of cyanogen azide, NCN_3 , and detected by a narrow-bandwidth UV difference laser absorption setup at a wavelength of 329.1302 nm [2]. The CN radical yield of the NCN + NCN self-reaction has been investigated by additionally detecting CN in its red band at a wavelength of 622.2733 nm by means of a sensitive 1 GHz frequency modulation setup.

Modeling of a rich methane flame reveals that the radicals CH_3 and OH appear in comparable and high mole fractions in the reaction zone. Until now, the rate constants of the reactions $\text{NCN} + \text{CH}_3$ and $\text{NCN} + \text{OH}$ have only been addressed theoretically. Here, we present an experimental study based on NCN and OH detection, the latter monitored at a wavelength of 310.2131 nm. The precursor *tert*-butyl hydroperoxide (TBHP) was used as a quantitative source for both CH_3 and OH. In agreement with recent theoretical work, the OH reaction turns out to be slow, whereas the $\text{CH}_2\text{NH} + \text{CN}$ forming reaction with CH_3 proceeds close to the collision limit.

The reaction $\text{NCN} + \text{H}$ is lifetime-limiting for NCN and its branching determines the overall chemical pathways for prompt-NO formation. In particular, the transition temperature for the branching ratio of the two main channels $\text{CH} + \text{N}_2$ and $\text{HCN} + \text{N}$, the so-called prompt-NO switch, remains a topical subject. For the first time, the yield of the $\text{HCN} + \text{N}$ channel has been experimentally measured by recording HCN concentration-time profiles. Recent developments of highly efficient electro-optic modulators working in the mid-IR range enabled the so far pending detection of HCN using a new 489 MHz frequency modulation spectroscopy setup. HCN mole fractions as low as 3 ppm ($T = 1000 \text{ K}$, $p = 0.4 \text{ bar}$) could be detected taking advantage of a strong rovibrational transition at 3097.846 nm (3228.049 cm^{-1}) [3]. For the investigation of the reaction $\text{NCN} + \text{H}$, the well-known thermal decomposition of ethyl iodide served as a reliable source for H atoms, and a dual NCN/HCN detection ensured a consistent evaluation of the channel branching to $\text{HCN} + \text{N}$.

[1] N. Lamoureux, P. Desgroux, M. Olzmann, G. Friedrichs, *PECS* **2021**, 87, 100940.

[2] N. Faßheber, L. Bornhorst, S. Hesse, Y. Sakai, G. Friedrichs, *JPC A* **2020**, 124, 4632–4645.

[3] M. Stuhr, S. Hesse, G. Friedrichs, *Fuels* **2021**, 2, 437–447.