Resolving NCN radical networks - The prompt-NO switch

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The spectroscopy, thermochemistry, and high-temperature kinetics of the NCN radical has attracted considerable attention after it has been recognized that the famous Fenimore prompt-NO initiation reaction $^2CH + N_2$ does not yield the spin-forbidden textbook products HCN + ^4N, but – according to M. C. Lin – follows the until then unidentified spin-allowed reaction pathway forming ^2H + ^3NCN. The study of NCN kinetics and the necessary implementation of NCN chemistry into detailed NO_x formation models for hydrocarbon combustion turned out to be both challenging and interesting. Over the years, various debates arose about seemingly easy to measure or calculable quantities such as the enthalpy of formation and absorption cross section of NCN that need to be accurately known for a reliable interpretation of the experimental results. In fact, the investigation of the spectroscopy, electronic structure, and reactivity of NCN has many facets as both spin states, NCN ($^1\Delta_g$) and NCN ($^3\Sigma^+$), need to be considered. Whereas chemical and photochemical production of NCN (e.g., by thermal decomposition or UV photolysis of cyanogen azide, NCN_3) yields the excited singlet state, in thermal systems the reactivity of NCN is dominated by the triplet ground state radical in most cases. As such, the study of NCN reactions also touches the topic of electronic deactivation and relaxation mechanisms. Recently, the "story of the NCN radical" and its role for prompt-NO formation has been reviewed by Lamoureux et al. [1] Here, the concept of the prompt-NO switch (i.e., essentially the switching of the product branching ratio of the key reaction ^3NCN + ^2H) has been highlighted, which serves as a temperature (and pressure) dependent knot in the complex network of NCN reactions in flames. Whereas toward low temperatures the switch is on $^2CH + N_2$ as the products of a recombination-initiated pathway taking place on a doublet potential energy surface (corresponding to the reverse of the prompt-NO Fenimore initiation reaction), toward higher temperatures the switch flips over to the activation-controlled reaction products HCN + ^4N on a quartet surface (corresponding to the products of the traditional Fenimore route to prompt-NO). Interestingly, most recent high-level computational results locate the related prompt-NO switch temperature to 3200-3400 K, whereas experimental findings are consistent with 1400-1600 K – hence predicting a just opposite switch position at combustion relevant temperatures!

This talk aims to provide an overview of the current understanding of prompt-NO formation, with a focus on spectroscopic, diagnostic, and reaction kinetic aspects related to ^1NCN and ^3NCN. New rate constant data on the so far overlooked radical cross reaction $^3NCN + {}^2CH_3$ as well as results of a first direct measurement of the branching ratio of the reaction ^3NCN + ^2H will be presented, hopefully resolving the issue of the prompt-NO switch temperature.

[1] N. Lamoureux, P. Desgroux, M. Olzmann, G. Friedrichs. Progress in Energy and Combustion Science 87 (2021) 100940/1-34.