

4D10: EXPERIMENTS AND MODELING OF IGNITION DELAY TIMES, FLAME SPEED AND INTERMEDIATE SPECIES OF EHN-DOPED STOICHIOMETRIC *n*-HEPTANE/AIR COMBUSTION.

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**Comment by William H. Green, MIT, USA**

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There is a chain mechanism for NO<sub>x</sub> to generate radicals: NO<sub>2</sub> + RH = HONO + R  
HONO + M = OH + NO + M NO + HO<sub>2</sub>(or RO<sub>2</sub>) = OH(or RO) + NO<sub>2</sub> at each cycle of the chain two radicals are generated and one unreactive HO<sub>2</sub> radical is converted into an OH. Note that the chain is fastest if there is an RH with a weak C-H bond in the mixture, e.g. CH<sub>2</sub>O. At very high NO<sub>2</sub> concentrations, OH + NO<sub>2</sub> → HONO<sub>2</sub> is a deactivating step, but probably this situation does not occur in your system. Does your model incorporate all the steps in this chain? If so, is the chain operative under your reaction conditions (i.e., chain length > 1)?

**Reply by Michaela Hartmann**

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Step I (NO<sub>2</sub> + RH = HONO + R) is included, for RH = *n*-heptane [1]. It is not included for the case RH = CH<sub>2</sub>O. Note that, in the phase where CH<sub>2</sub>O is present in significant amounts, many other reaction paths are very fast, rendering the NO<sub>2</sub> + RH = HONO + R path less important. Step II (HONO decomposition) is included according to HONO = OH + NO. Step III (NO + HO<sub>2</sub> = OH + NO<sub>2</sub>) is included, while the deactivation step IV (OH + NO<sub>2</sub> = HONO<sub>2</sub>) is not included. We have performed simulations with reactions I–III included in the mechanism and also with these reactions excluded; there was only a marginal difference in the resulting ignition delay times. We therefore conclude that, for the range of conditions investigated in our work, the chain is of no significant influence for the ignition delay times.

Reference:

[1] W.T. Chan, S.M. Heck, H.O. Pritchard, *Phys. Chem. Chem. Phys.* 3, (2001) 62–65.