Detailed kinetic modeling of allene pyrolysis and combustion

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This paper focuses on the development a reaction kinetic mechanism for allene and propyne sub-mechanisms on the DLR reaction data base. The detailed chemistry of allene and propyne is a part of earlier published C_2 mechanism [1] with polyaromatic hydrocarbon (PAH) formation.
The allene oxidation, pyrolysis and combustion sub-mechanism was validated and analyzed beginning which simulations of experimental data for ignition delay times [2,3], laminar flame speeds [4] and species concentration profiles [5-7] with kinetic schemes [1]. Simulation results shown, that the DLR mechanism generally describes the allene oxidation. The modelling results match the ignition delay experimental data quite well at high temperatures, but significantly disagree with measured data as low temperatures.
Sensitivity analyses have been carried out to identify the most important reactions for the development of the oxidation reaction chain. After selection of these reactions, the analysis of their rate coefficients was performed. The rate constants recommended in literature from various sources have been treated with a least-squares regression [8] to evaluate the uncertainty range. Fig. 1 shows an example of such a treatment. For the reactions $C_3H_4 + H = H_2CCCH + H_2$ and $C_3H_4 + H = CH_3 + C_2H_2$, different rate constants were used in the approximation and the estimated total uncertainty area determined.

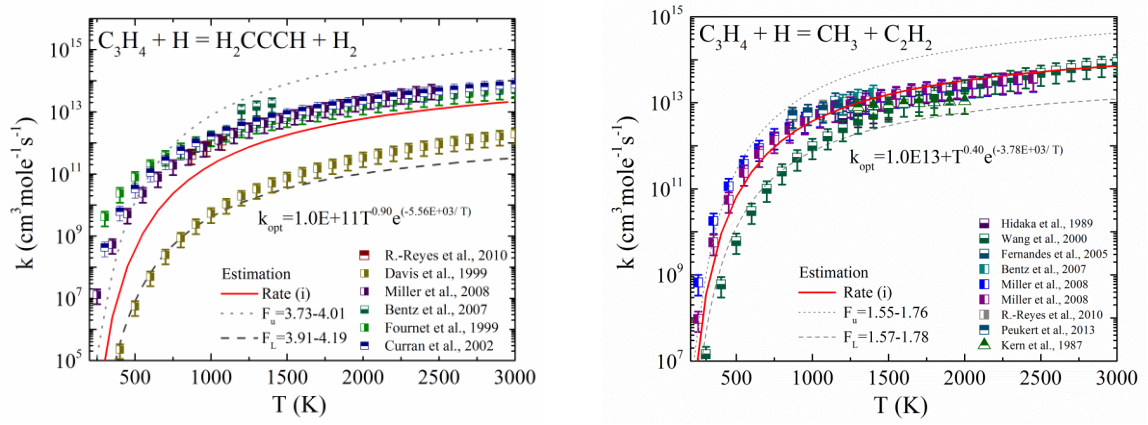

Fig. 1 The uncertainty boundary evaluations for reaction rate constants for $C_3H_4 + H = H_2CCCH + H_2$ and $C_3H_4 + H = CH_3 + C_2H_2$ over temperature range of 300-3000 K.

The obtained uncertainty factors determine the range of coefficient optimization through simulations of the experimental data in order to improve the agreement with the experimental data. The ignition delay times and laminar flame speed data have been used for improvement of general oxidation reaction paths, Fig.2.
The suitability of the mechanism used to investigate the pathways of the formation of polyaromatic precursors was studied and improved on the basis of modelling the concentration profiles of the main and intermediate combustion products allene and propyne, Fig 3.

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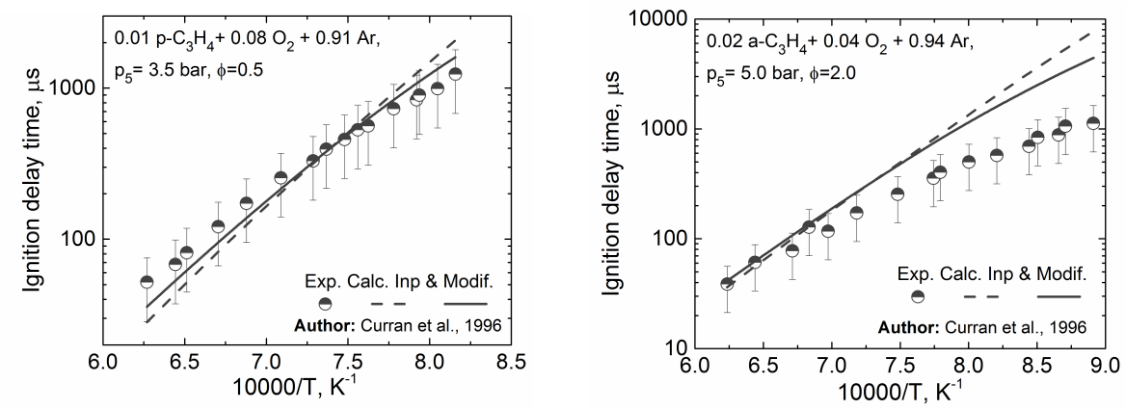

Fig.2. Experimental (symbol) [2] and computed (line) of the ignition delay time of allene-oxygen-argon flame at high- and low- temperature.

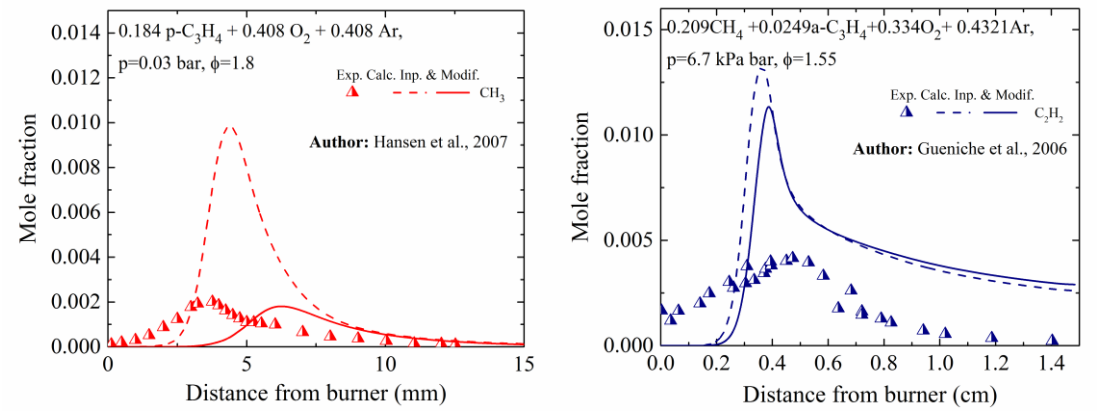

Fig.3. Experimental (symbol) [5,7] and computed (line) mole fraction profiles of CH_3, C_2H_2 in allene (methane/allene)-oxygen-argon flame.

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