

EXPERIMENTAL AND MODELING STUDIES OF THE COMBUSTION OF LOW MOLECULAR WEIGHT UNSATURATED HYDROCARBONS

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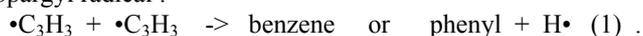
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During the last decade, several experimental and theoretical studies have been attempted in order to understand how polycyclic aromatic hydrocarbons (PAHs) are produced during the combustion of hydrocarbons. It is now well established that PAHs are soot precursors and that the formation of single aromatics like benzene can be considered as a crucial stage in the mechanism of particles production. Thus, over the past few years, several reaction pathways and submechanisms have been proposed for modeling benzene formation, especially for small unsaturated species (acetylene, ethylene, ...), at high temperature in premixed flames or shock tube experiments (Wang et al. [1], Bastin et al. [2], Westmoreland et al. [3], Miller et al. [4]). Recently, our laboratory has developed a software (EXGAS) which permits to generate automatically detailed oxidation or combustion mechanisms for paraffins and iso-paraffins [5,6]. These generated oxidation mechanisms can contain primary molecules as butene, propene, ethylene and secondary molecules as 1,3-butadiene or acetylene which can be considered as precursors in the formation of benzene at high temperature. However, due to the large number of species and specific reactions involved in the formation of aromatics, it seems difficult and useless to include in EXGAS generic reactions in order to take into account the formation of aromatics from small unsaturated species. The development of a reaction data base which can be added to detailed mechanisms produced by EXGAS seems to be the best way to describe the formation of aromatics during the oxidation of large hydrocarbons.

In a first part of this paper, we describe an experimental and modeling study of the oxidation of acetylene, propyne and 1,3-butadiene in shock tube and we discuss the ignition delays measured. In a second part, we compare our simulations and experimental results obtained in a premixed laminar 1,3-butadiene flame [7].

Autoignition delays were measured in a stainless steel shock tube; the reaction and the driver parts were respectively 400.6 and 89 cm in length and were separated by two terphane diaphragms. These diaphragms were ruptured by decreasing suddenly the pressure in the space separating them. The driver gas was helium. The incident and reflected shock velocities were measured by piezo-electric pressure transducers located along the reaction section. The state of the test gas behind the incident and the reflected shock waves was derived from the value of the incident shock velocity by using ideal one-dimensional shock equations. The onset of ignition was detected by OH radical emission at 306 nm through a quartz window with a photomultiplier fitted with a monochromator at the end of the reaction part. The ignition delay time was defined as the time interval between the pressure rise due to the arrival of the reflected shock wave and the rise of the optical signal by the photomultiplier up to 10% of its maximum value. The following experimental conditions have been used : temperatures ranging from 1000 to 1650 K, pressures ranging from 8.5 to 10.0 atm and mixtures (argon : hydrocarbon : oxygen, in molar percent) were respectively (91 : 1 : 8), (95 : 1 : 4) and (85 : 3 : 12).

A reaction base (C₃-C₆ reaction base) has been built from a review of the recent literature and is a development of the C₀-C₂ reaction base developed in our laboratory by Barbé et al. in 1995 [8]. We added to this previous base the reactions of the main C₃-C₄ unsaturated molecules and radicals, as well as the formation of benzene at high temperature. The formation of benzene through a C₄ pathway, as proposed mainly by Wang et al. [2] or Westmoreland et al. [3], has been written. In this pathway, the aromatic ring is formed by considering the addition of acetylene to n-C₄H₃• and n-C₄H₅• radicals followed by a cyclisation to give benzene or phenyl radical. Taking into account the work of Miller et al. [4] concerning the flame of acetylene, we have also considered the stabilized radicals i-C₄H₃• and i-C₄H₅•. A second pathway for the formation of benzene has been more recently proposed by several authors [4] and was adopted in our mechanism. This channel is related to the recombination of propargyl radical :



Even if this process is relatively complicated and imply multiple isomerizations, it seems that experimental observations have corroborated this hypothesis. By analogy with reaction (1), we also considered the combination of a propargyl with an allyl radical, $\alpha\text{-C}_3\text{H}_5\cdot$ [9]. The last channel concerns Diels Alder reactions and especially the reactions of 1,3-butadiene with ethylene or acetylene, followed by successive dehydrogenation of the cyclohexene or cyclohexadiene formed. In addition to benzene formation pathways, reactions involving $\text{C}_3\text{H}_2\cdot\cdot$, $\cdot\text{C}_3\text{H}_3$, C_3H_4 (allene and propyne), $\cdot\text{C}_3\text{H}_5$ (three isomers), C_3H_6 , C_4H_2 , C_4H_4 , C_4H_6 (1,3-butadiene, 1,2-butadiene, methyl-cyclopropene, 1-butyne and 2-butyne) have been considered from a systematic analysis of reactions found in the literature. However, due to a lack of reaction and kinetic data, it has not been possible to build this data base in a way as comprehensive as in the case of the $\text{C}_0\text{-C}_2$ reaction base.

Figures 1, 2 and 3 compare computed and experimental ignition delays obtained respectively with acetylene (fig. 1), propyne (fig. 2) and butadiene (fig. 3) and show that the agreement obtained is globally satisfactory. Figure 4 compares simulated profiles with the experimental results obtained by Cole et al. in a flame of 1,3-butadiene [7]. For all the species measured, the agreement is satisfactory. A key points of our simulations is that they have all been performed by using the same mechanism, i.e. the $\text{C}_0\text{-C}_6$ reaction base previously described, without any adjustment of kinetic data. These simulations have been run by using the CHEMKIN II software library. For all the unsaturated hydrocarbons studied, the flow rate analysis have been performed and have permitted to give the channels, important in shock tube or flame conditions.

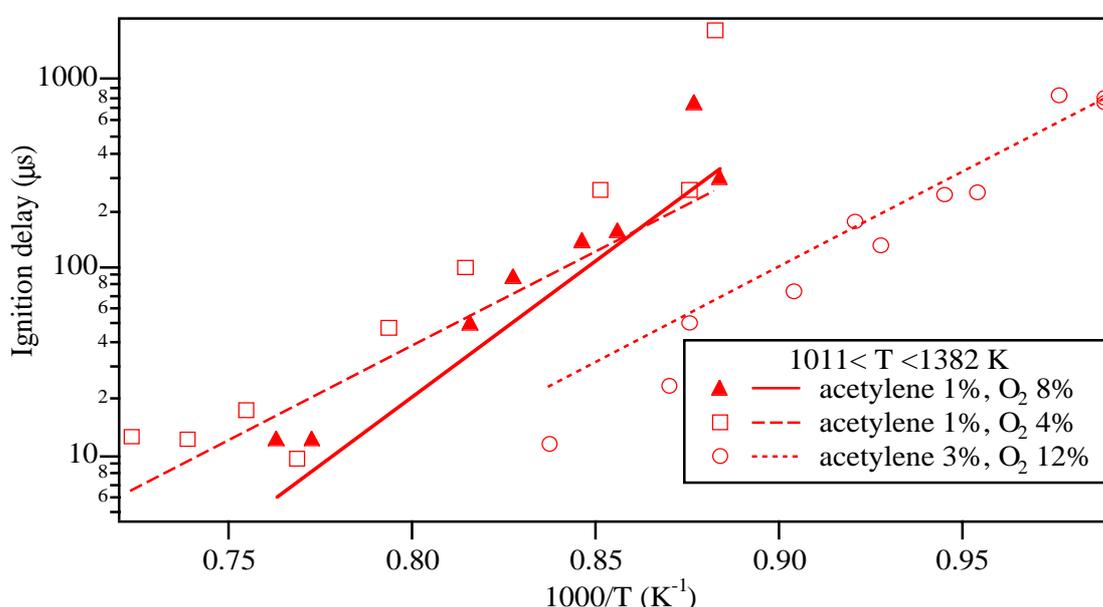


Figure 1: ignition delays of acetylene versus temperature. Points correspond to experimental results and lines to simulations.

Acetylene react mainly by additions. Additions of $\cdot\text{O}\cdot$ atoms on the triple bond lead to the formation of CO and $^3\text{CH}_2\cdot\cdot$ or of $\cdot\text{CHCO}$. Additions of $\cdot\text{H}$ atoms produce vinyl radicals. Vinyl radicals can react with oxygen by two channels. One of these channels involves the formation of $\cdot\text{CHO}$ radicals and formaldehyde; the second channel is a branching step producing $\cdot\text{O}\cdot$ atoms and $\cdot\text{CH}_2\text{CO}$ radicals. Sensitivity analyses show that this branching step and the fast initiation reaction between acetylene and oxygen explain the high reactivity of acetylene-oxygen mixtures, which has been observed in a shock tube. In flames above 1400 K, the addition of $^3\text{CH}_2\cdot\cdot$ would also need to be considered. This addition leads to the formation of propargyl radicals, whose recombination is important to explain the production of benzene. The major consumption channels of propargyl radicals in flames are reactions with $\text{OH}\cdot$ radicals leading either to $\text{C}_3\text{H}_2\cdot\cdot$ and H_2O or to $\text{C}_2\text{H}_3\cdot$ and $\cdot\text{CHO}$ radicals. In these conditions, vinyl radicals can also react by metathesis with formaldehyde and produce ethylene.

In the case of propyne, isomerization leading to allene is the most important reaction channel according to flow rates analysis. Nevertheless, in the time preceding auto-ignition, equilibrium is not yet reached and ignition delays are not very sensitive to the rate constant of this isomerization. Propyne react mainly by metatheses to give propargyl radicals. Major consumption reactions of allene include the addition of $\cdot\text{O}\cdot$ or $\text{H}\cdot$ atoms and its dimerization leading ultimately to C_2H_4 and C_4H_4 . Ignition delays are very sensitive to the rate

constants of the initiation reactions leading to H• atoms and propargyl radicals. Major consumption channels of propargyl radicals in these conditions are their reaction with oxygen leading to •CH₂CO and •CHO radicals and their recombination; propargyl radicals can also react with allene to give H• atoms and benzene.

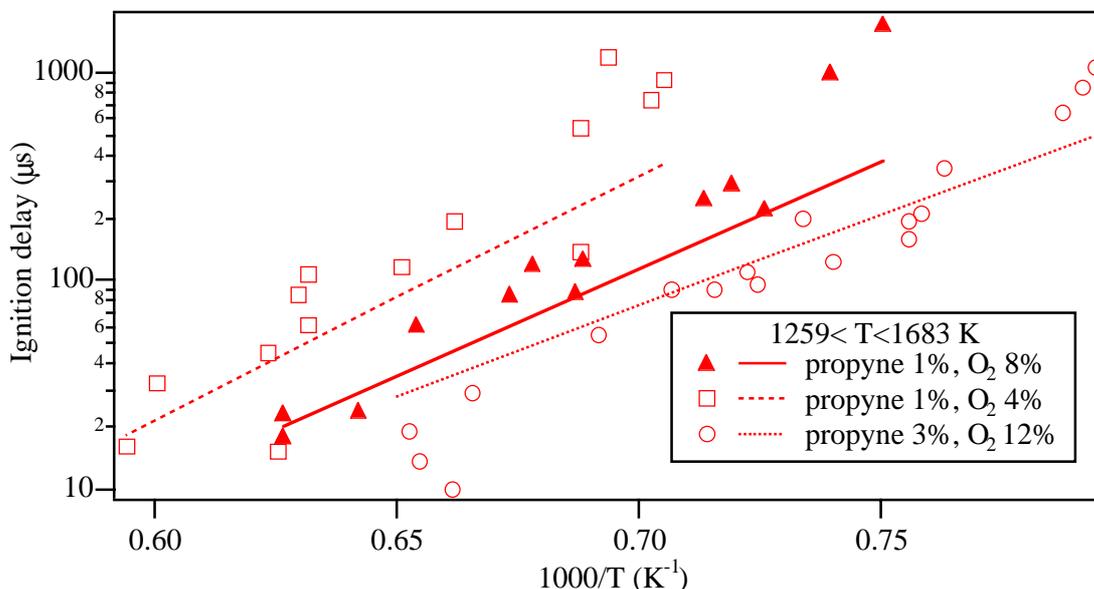


Figure 2 : ignition delays of propyne versus temperature. Points correspond to experimental results and lines to simulations.

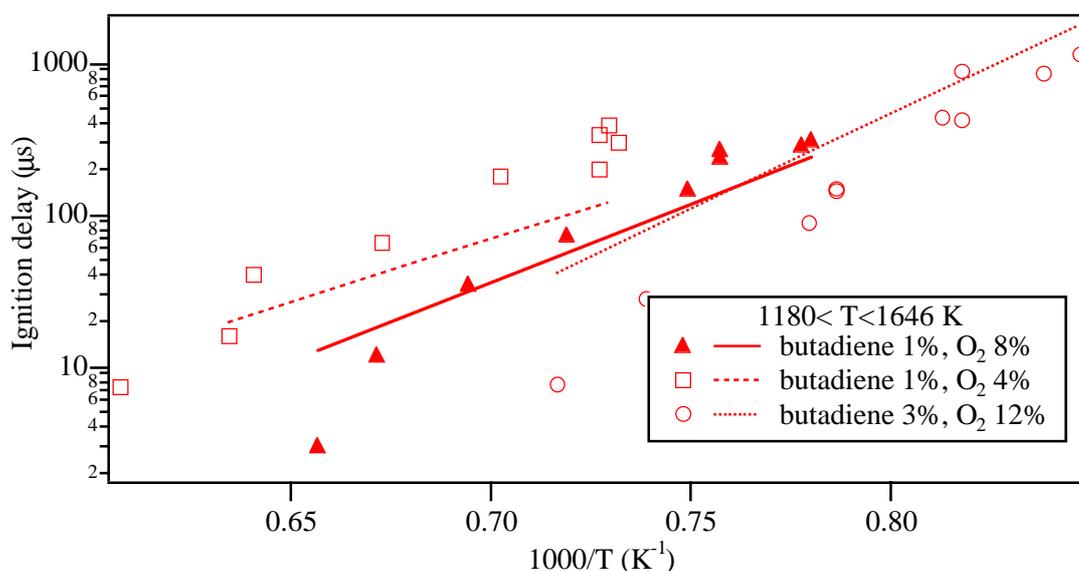


Figure 3 : ignition delays of butadiene versus temperature. Points correspond to experimental results and lines to simulations.

In the low temperature region of the flame ($T=750$ K), butadiene reacts mainly by OH• additions leading to aldehydes, such as acroleine ($\text{CH}_3\text{CH}_2\text{CHO}$); at higher temperatures, metatheses become preponderant. In the shock tube, major reactions include also •O• addition and isomerization. Unimolecular reactions are always more important in shock tubes than in flames because of the important dilution used during the determination of ignition delays. Metatheses lead to the formation of $n\text{-C}_4\text{H}_5\bullet$ and $i\text{-C}_4\text{H}_5\bullet$ radicals. The main reactions of $n\text{-C}_4\text{H}_5\bullet$ are their decomposition in acetylene and vinyl radicals and the reaction with oxygen. The resonance stabilized $i\text{-C}_4\text{H}_5\bullet$ radicals are mainly consumed by reaction with oxygen; one channel of this reaction is the main way of formation of C_4H_4 . In the case of butadiene, ignition delays are not very sensitive to the rate constant of initiation reactions; the most sensitive parameters are the rate constants of metatheses forming the not very reactive $i\text{-C}_4\text{H}_5\bullet$ radicals.

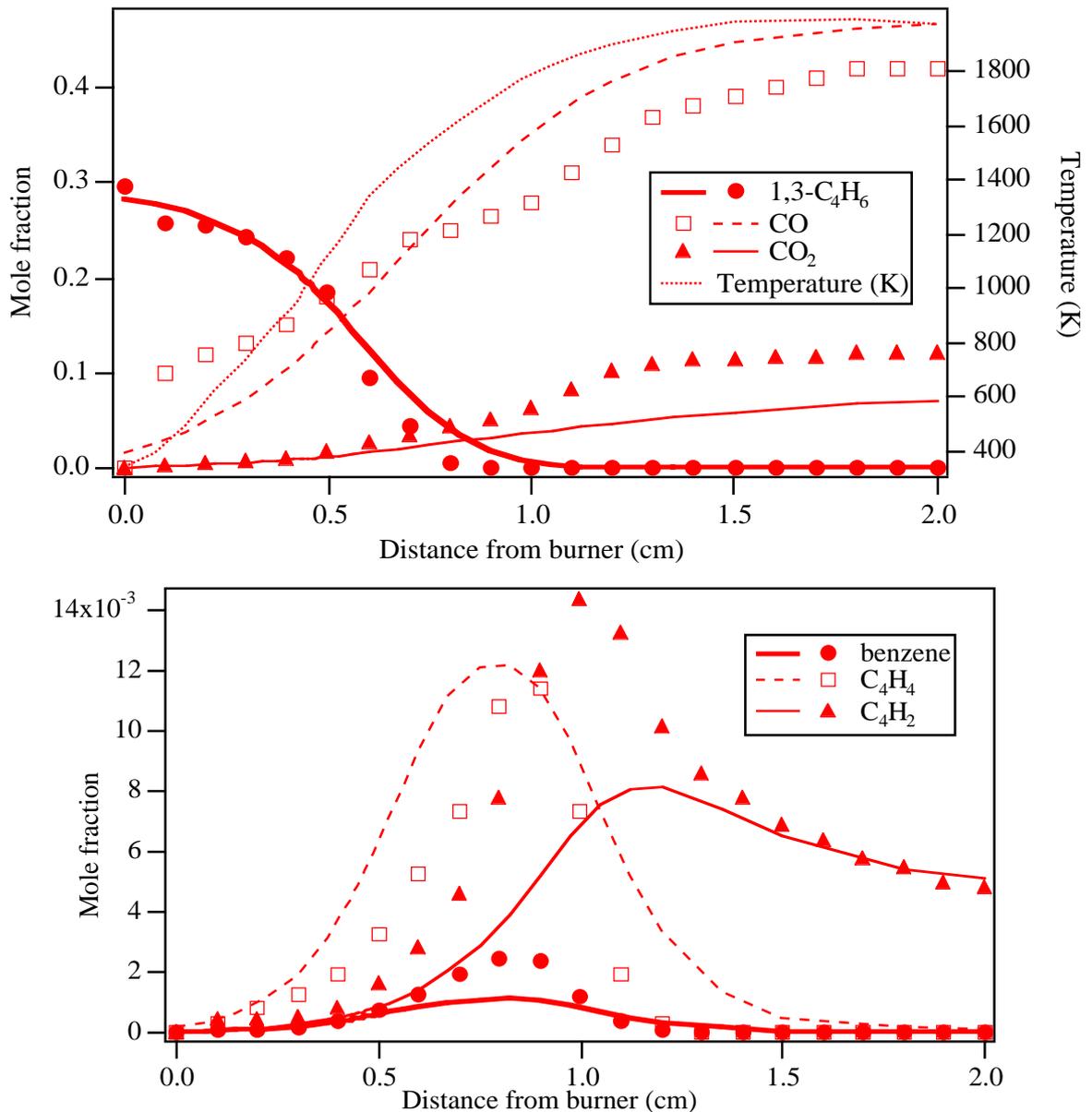


Figure 4 : Mole fraction in function of the distance from burner in an 1-3 butadiene laminar premixed flame. Points correspond to experimental results and lines to simulations.

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