

Detailed kinetic modeling of Polycyclic Aromatic Hydrocarbons formation in propane pyrolysis at high temperature/low pressure

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Abstract

Most of the works on PAH pathways formation are based on combustion processes studies ; however complementary works on PAH formation can be also developed by studying pyrolysis of hydrocarbons. That's why this work describes an experimental and modelling study of the pyrolysis of propane. The pyrolysis is carried out in a perfectly stirred reactor and in a wide range of temperature (1173K-1298K) and residence time (0,5-4s). During the pyrolysis, 29 products (hydrocarbons up to pyrene) are analysed by Gas-Chromatography. A detailed kinetic mechanism for the pyrolysis of propane is proposed, in order to reproduce the experimental gaseous species. The validation of the mechanism is performed by simulations and comparisons with experimental data. Main reaction paths of PAH formation are determined by flux analysis and underline the significant roles of resonantly stabilized radicals.

Introduction

A better understanding of Polycyclic Aromatic Hydrocarbons (PAH) is of practical interest because of their effects on health and on environment. Nowadays, the main studies on PAH formation are carried out in oxidation condition [1-6]. However, PAH are also generated by industrial pyrolysis processes. That's why a complementary work on PAH formation can be also developed by studying pyrolysis of hydrocarbons.

During the last few years, a significant number of experimental and modeling studies were carried out in order to improve the knowledge of the detailed kinetic reactions involved in the hydrocarbon pyrolysis. Until to now, just a very few number of partial models have been proposed in the literature with [7] or without [8-10] qualitative validations. So, no detailed kinetic mechanism allows to reproduce quantitatively the concentration of the species in the gas phase during the pyrolysis. The main purpose of this study is to propose a detailed and validated kinetic mechanism for the pyrolysis of propane in order to reproduce the gas phase species and more especially the PAH.

In the first part of this paper, we will present the experimental apparatus developed to study the pyrolysis of propane in a self-stirred reactor. Then the detailed mechanism for the pyrolysis of propane will be described. Comparisons between experimental and theoretical results, concerning the PAH, will be shown in another section, and completed by a kinetical analysis of the pathways leading to the formation of PAH.

Experimental method

The pyrolysis of propane is performed in a specific perfectly stirred reactor. It is self-stirred by gas jets and works at a steady flow, isothermal, isobar and isochoric conditions, in the range of space times : 0.5-5 seconds

and around 1273 K. The reactor made in quartz, is shown figure 1. It has been designed to examine both gas phase reactions and surface processes. More details and comments on this reactor are given in a specific paper [11].

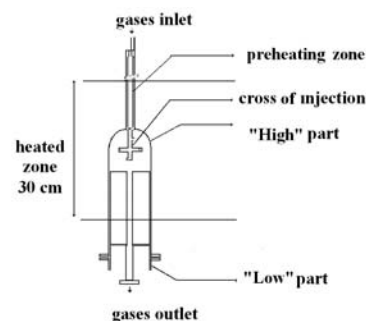


Fig. 1 : Jet Stirred Reactor

This reactor is adapted from the spherical jet-stirred gas phase reactor developed by Matras and Villermaux [12], and largely used in investigations of gas phase reactions [eg 13-14]. The reactor is composed of two parts, which are connected one to the other. The "high" part includes an annular pre-heating (interannular distance = 0.5 mm) directly connected to a cross of injection, placed at the center of the reactor. The reactants are preheated at the reaction temperature in the annular exchanger in a short time compared with the reaction time [13]. The cross is composed of four nozzles, which produce a jet in different directions and ensure the mixing of all the volume of the reactor. The upper extremity is half spherical and the lower part is designed to be connected to a cylindrical support ("low" part in Fig.1). The circular support is bored in its center for the output of gas and sampling for analyse. The free volume of the

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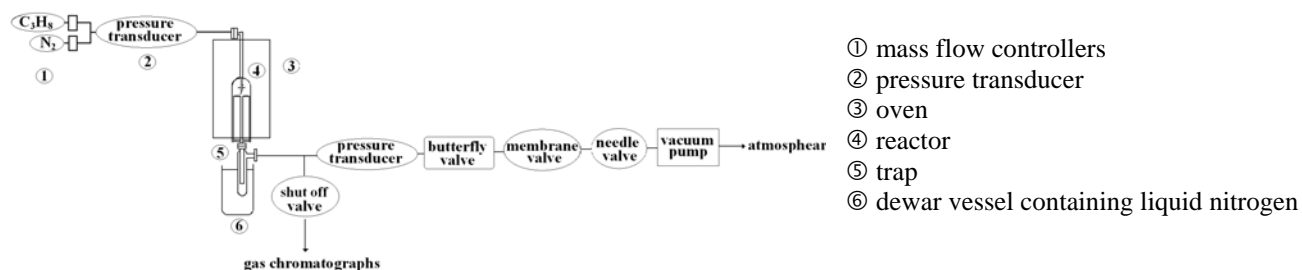


Fig. 2 : Experimental apparatus

reactor is approximately 90 cm^3 and the internal area is 100 cm^2 .

Most experimental results reported in the pyrolysis of hydrocarbons have been obtained with tubular reactors, which presents the drawback of generating a profile of species concentration along its axis [15-17]. So, it is not possible to know precisely the composition of the gas phase during the pyrolysis. The knowledge of the quantitative composition of the gaseous phase is essential to write and quantitatively validate a mechanism of propane pyrolysis.

The experimental apparatus of pyrolysis (fig. 2) permits to vary several parameters : the reaction temperature, the total pressure in the reactor, the nature of the mixture, the residence time of gases in the reactor. All the experimental data presented here has been obtained under the following experimental conditions : a total pressure in the reactor of 2,7 kPa (0,35 kPa of propane diluted in nitrogen), a temperature ranging from 1173K to 1298 K, and a residence time ranging from 0,5 to 4 seconds.

Concerning the products of propane pyrolysis, the light products containing less than five atoms of carbon are taken at the outlet of reactor and analysed on-line. Their quantification is realized by two gas chromatographs placed in series, and the products analysed are the following : hydrogen, methane, ethane, ethylene, acetylene, propene, propyne, propadiene, butene, butadiene, but-1-ene-3-yne, 1,3-butadiyne. The first chromatograph is a "Shimadzu GC 14" equipped with a TCD and FID detectors. Hydrogen, methane, and C_2 -hydrocarbons are separated using a filled-column "Carbosphere" (Alltech). The second chromatograph is a "Hewlett Packard 6850" using a FID detector. On this GC, C_2 , C_3 , C_4 -hydrocarbons are analysed. A large-bore $530\mu\text{m}$ column "GS Alumina" (J&W scientific) is used to separate the products. Nitrogen has been used as carrier gas in both cases.

The heavy species (starting from 5 carbon atoms) are condensed at the outlet of reactor in a cooled trap with liquid nitrogen during 4 hours. They are dissolved in 5 mL of acetone to be analysed by gas chromatography with a "Shimadzu GC-17" equipped with a FID detector. For the separation of products a capillary column "HP5" (5% phenyl-95% dimethylpolysiloxane) is used. Nitrogen has been also used as carrier gas.

The 17 following heavy species are quantified : cyclopentadiene, benzene, toluene, ethylbenzene, p-xylene, phenylacetylene, phenylethylene, indene, methyl-naphthalene (1 and 2), naphthalene, biphenyl, phenanthrene, anthracene, pyrene, acenaphthylene, fluoranthene. Only the major products have been analysed but other minor species were also identified by GC-MS with a HP G1800A GCD system. [18]

Modelling of propane pyrolysis

As previously discussed, the radical reactions involved in the pyrolysis of propane lead to the formation of many gaseous species, from hydrogen up to heavy PAH such as benzofluoranthene. In order to reproduce their concentrations quantitatively, it is necessary to develop a detailed mechanism based on elementary reactions [19, 20]. These elementary reactions, taken into account in the pyrolysis of propane, derive primarily from other studies on the oxidation of hydrocarbons in our laboratory [21-23].

Our mechanism can be divided in four submechanisms. The primary mechanism of the pyrolysis of propane describes only the pyrolysis of the reactant. The kinetic data are primarily those proposed by Tsang for the oxidation of C_3H_8 or those used in the modeling of the oxidation of alkane [24, 25].

The C_0 - C_2 reaction base includes all the unimolecular or bimolecular reactions involving radicals or molecules containing less than three carbon atoms. The kinetic data used in this base were taken from the literature and are mainly those proposed by Baulch et al. [26] and Tsang et al. [27]. This base derives mainly from previous oxidation studies [23, 28].

The C_3 - C_7 reaction base described the main reactions of C_3 - C_5 unsaturated molecules and radicals as well as the formation of benzene and toluene. The reactions involving C_3 - C_4 unsaturated species are mainly those proposed in previous studies in our laboratory [22-25]. The reactions involving C_5 species have been added to the mechanism due to their role in the formation of aromatic and polyaromatic species. Notably, these reactions take into account the formation of cyclopentadiene observed experimentally. The formation of benzene through a C_4 pathway, as proposed mainly by Wang et al. [5] or Wesmoreland et al. [29] has been written, by considering the addition of acetylene to $n\text{-C}_4\text{H}_3\cdot$ and $n\text{-C}_4\text{H}_5\cdot$ radicals followed by a cyclisation to give benzene or phenyl radical. A second

route for the formation of benzene and proposed by several authors [30-31] is related to the recombination of propargyl radical. Finally, a third pathway, proposed by Weissman and Benson [32] has been taken into account and is based on successive additions of methyl free radical on unsaturated molecules such as acetylene or propene, followed next by dehydrogenation and cyclisation to give C₆ ring closure. The formation of toluene has also been described mainly by two routes. The first one is the combination of methyl radical ·CH₃ with the phenyl radical ·C₆H₅ and the second one is an ipso addition between benzene and ·CH₃. A last pathway leading to the formation of toluene has been proposed by Marinov et al. [33] and involves reaction between stabilized free radicals derived from butadiyne and propargyl.

The C₈-C₁₈ reaction base described the main reactions of C₈-C₁₈ aromatic and polyaromatic molecules and radicals. They mainly comes from previous studies based on oxidation study. [1-6] Because heavy species mainly represent minor species

compared to little products as hydrogen or acetylene, only the “principal” routes of reaction have been written, this allows to keep a reasonable size for this mechanism. So, only unimolecular initiation leading to the formation of stabilized free radicals has been considered, because of the high activation energy involved in these reactions. Beta-Scission of C-C and C-H bonds have been taken into account in the mechanism. Due to the high activation energy involved in the breaking of a C-H bond, we only considered the case of the beta-scission of an allylic hydrogen atom (for which the activation energy is of the same order than for a scission of a C-C bond) and the beta-scission of hydrogen atom when no scission of a C-C bond (with a lower activation energy) is possible. The H-abstractions taken into account in the mechanism are those involving reactive free radicals as H atom, CH₃, vinyl radical (C₂H₃) but also, stabilized free radicals such as propargyl, allyl or cyclopentadienyl, which have a high concentration. These H-abstractions have been written only for important species. Because at high

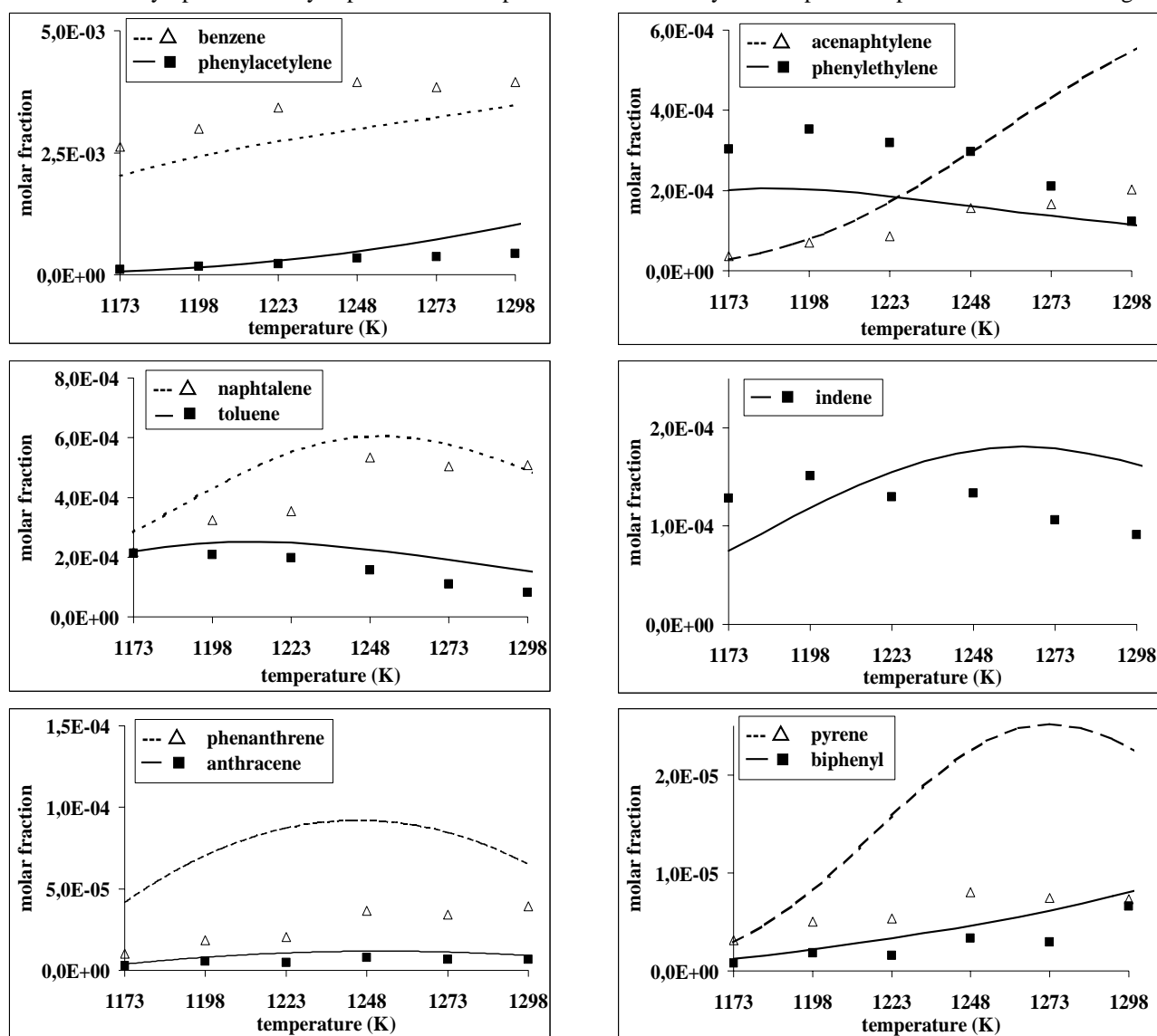


Fig. 3 : Comparison between experimental (symbols) and computed (lines) mole fraction of heavy species versus temperature. (P=2,7 kPa, residence time = 1 s)

temperature and low pressure, additions of free radicals on an unsaturated bond of a molecule are not favoured, the principal addition of free radicals involved major species i.e. acetylene, ethylene or propyne. Finally, terminations by combinations of free radicals with H or CH_3 radicals have always been considered in the mechanism. But they were also taken into account for important resonant free radicals because of their low reactivity and high concentration.

The kinetic data used in our mechanism were taken, mainly, from the literature (Baulch et al [26], Tsang et al.[24, 27], NIST data Base). Some kinetic data for the isomerizations of radicals, the recombination of free radicals and the unimolecular decompositions of molecules are calculated by a software, KINGAS, developed in our department by Bloch-Michel [34] and based on thermochemical methods. Correlations

obtained from a literature review are also used to estimate the kinetic data relevant to reactions involving species for which no data can be found in the literature ; it was especially the case for some reaction concerning the PAH. Because of the low pressure imposed by our pyrolysis conditions, some reactions involved in the pyrolysis can be pressure dependent, in particular for small species (C_0 – C_3). In order to take into account the fall-off, we tried to use kinetic parameters found in the literature and calculated at low pressure, or kinetic parameters using Troë's coefficients, which allow to calculate the corresponding kinetic data for each pressure value [35]. The thermochemical data, heats of formation, entropies and specific heats of molecules or radicals are mainly calculated by using a software (THERGAS), developed in our laboratory [36] or obtained from the literature. THERGAS is based on

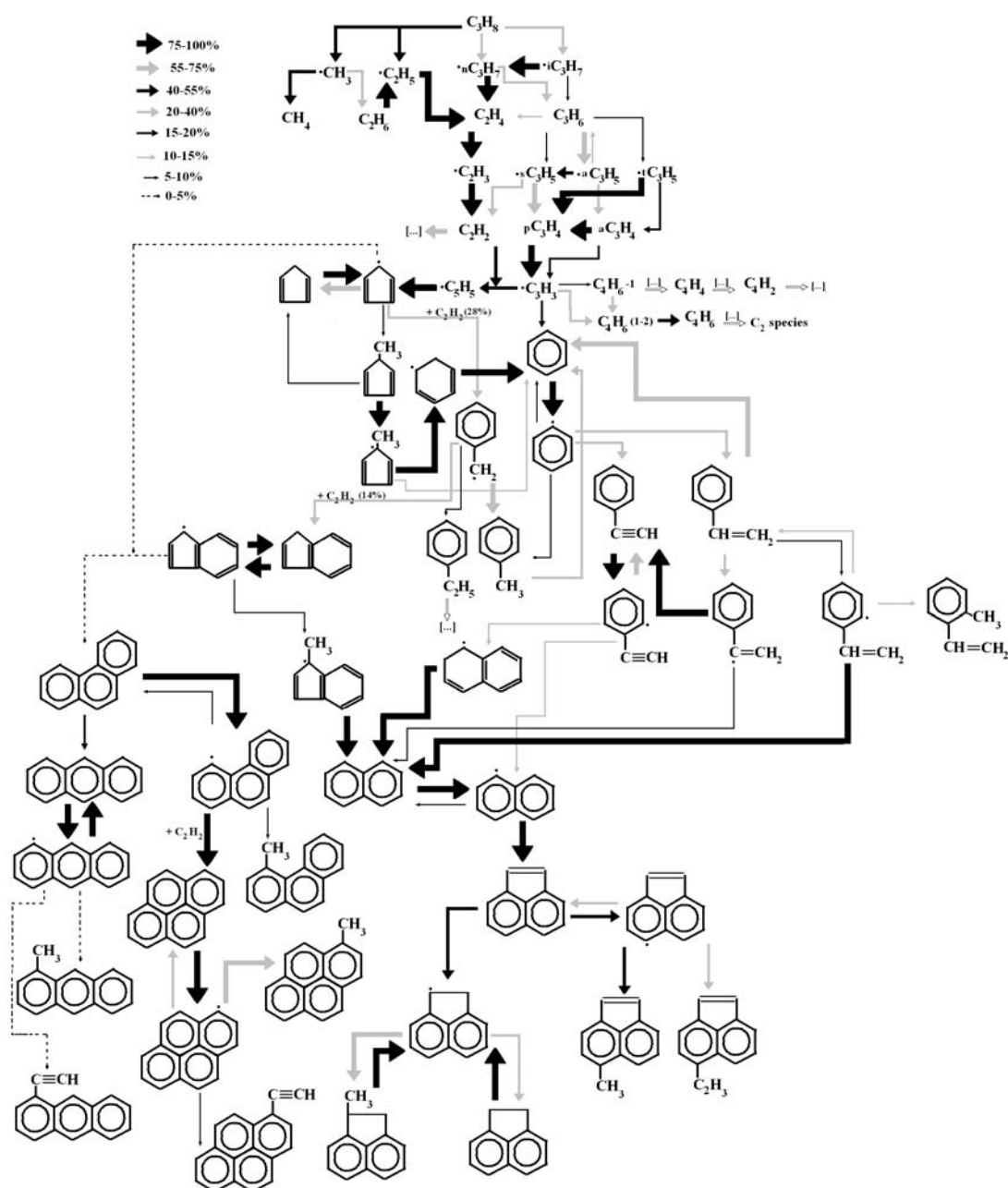


Fig. 4 : Flux analysis of propane pyrolysis ($T = 1248 \text{ K}$, residence time = 1 s)

statistical mechanics and group additivity methods proposed by Benson [37]. The thermochemical data of every molecular or radical species are automatically calculated and stored as 14 polynomial coefficients, according to the Chemkin II formalism [38].

Results and discussion

Simulations are performed with CHEMKIN II software [38] using the mechanism previously described. The same set of kinetic parameters has been used to perform all the simulations and to improve the agreement with experimental results. Figure 3 presents comparisons between the experimental results (symbols) and computed profiles (lines) according to the temperature. Only the modeling of PAH is presented here, the modeling of lighter species is correct and it is shown in another paper [19]. The experimental conditions were mentioned above.

The agreement is satisfactory for most of the aromatic and polyaromatic species. Thus, benzene, toluene, naphthalene, indene, phenylethylene, anthracene and biphenyl are well predicted. Phenylacetylene and acenaphthylene are overpredicted at high temperature. The heaviest species quantified, pyrene and phenanthrene, are overpredicted by our modeling, however only a part of their consumption is written.

A flow rate analysis has been performed, with the mechanism described previously at a temperature of 1248 K and a residence time of 1 second. Figure 4 presents the main routes involved in the PAH formation by propane pyrolysis. The arrows, expressed as a percentage, indicate the flow of consumption of a species.

This analysis allows to underline the importance of some reactional paths of PAH growth and importance of resonantly stabilized radicals. Indeed, the radical propargyl C_3H_3 appears as a very important intermediary because it is consumed to form three "families" of products; namely the " C_4 ", the by-products of benzene and those of cyclopentadiene. The radical cyclopentadienyl resulting from propargyl is itself a very important species because it is the forerunner of the formation of cyclopentadiene, indene, and thus naphthalene, acenaphthylene, phenanthrene and anthracene. So it intervenes very strongly in the formation of the "organized" aromatic polycyclic species which are not ramified. While the benzene evolves to ramified aromatic cycles such as phenylethylene, ethylbenzene, phenylacetylene or toluene. The stabilized radical indenyl is also important because it leads indirectly to the formation of naphthalene.

The formation of toluene can be described by two main routes. The first way of formation of toluene is the combination of radical phenyl with radical methyl but it is worth noting that only 4% of toluene come from this reaction. The second and most important way is the combination of radical benzyl with the radical H. Nevertheless benzyl is also formed by the addition of

radical cyclopentadienyl on acetylene. Thus, toluene is indirectly produced via radical cyclopentadienyl. It can be also notice that 29 % of toluene is consumed by an "ipso-reaction" in order to form benzene.

The addition of benzyl on acetylene is the main way of formation of indene. The radical indenyl is also important because it leads indirectly to the formation of naphthalene.

Indeed, naphthalene is mainly (82 %) produced by the reaction, which involves the methylindene. This reaction is close to those of isomerization between fulvene and benzene, since it allows the elimination of the "five-membered ring" in order to produce a new "six-membered" ring. It is worth noting that 9% of naphthalene come from the reaction, which involves the self-combination of two resonantly stabilized radicals cyclopentadienyl, [39]. Naphthalene is only consumed by H-abstraction to lead to the radical naphthyl.

Naphthalene, via the addition of radical naphthyl on acetylene, evolves to the formation of acenaphthylene, which is also a major experimental heavy species of propane pyrolysis. More than 95% of acenaphthylene come from this reaction, and underline the importance of the addition of acetylene in our experimental conditions.

Phenanthrene comes mainly from the reaction between two resonantly stabilized radicals cyclopentadienyl and indenyl. This reaction has been proposed Marinov et al. [1] by analogy with a reaction which allows the transformation of two "five-membered ring" into two "six-membered ring". Another minor pathway contributing to the formation of phenanthrene is the reaction of acetylene with biphenyl radical; it can be noticed that this route is proposed to be the main pathway of phenanthrene formation in several oxidation studies [2,5].

Finally, phenanthrene leads to anthracene by isomerization, but also leads to the formation of the pyrene, which is the heaviest quantified species. This last reaction shows again the importance of the addition of acetylene in the growth of PAH.

Conclusion

A detailed kinetic model of the propane pyrolysis, involving 608 reactions and 172 species, is proposed in order to reproduce some of the experimental gas phase species from methane up to pyrene.

In order to validate this mechanism, a quantitative experimental study of the propane pyrolysis at high temperature (1173K-1298K) and low pressure (2,7 kPa) has been carried out in a self stirred reactor. The propane pyrolysis has been studied on a wide range of temperature (1173K-1298K); it has allowed, by gas-chromatography, the quantification of more than 25 light and heavy species from methane up to pyrene ($C_{16}H_{10}$). Besides more than 30 other species, up to benzofluoranthene ($C_{20}H_{12}$) were also identified by mass-spectroscopy.

Most of the results obtained by modelling correctly reproduce the experimental results on a wide range of

temperature. It is worth noting that this agreement has been obtained with the same set of kinetic parameters.

In order to scheme the route of the propane pyrolysis, a flow rate analysis was also performed at 1248K for a residence time of 1 second (Fig. 4). The results have shown the importance of several pathways for the formation of PAH. Besides, the importance of resonantly stabilized radicals such as cyclopentadienyl, indenyl has been underlined. Afterwards, this analysis has shown the importance of the reactions involving the elimination of a "five-membered ring" on behalf of the formation a "six-membered ring". Finally, this study has shown again, as it was the importance of the reaction of acetylene addition, at least, in our conditions.

References

- [1] N. M. Marinov, W. J. Pitz, C. Westbrook, A. N. Vincitore, M. J. Castaldi, S. M. Senkan, *Comb. Flame*, 114 (1998) 192-213
- [2] H. Richter, W. J. Grieco, J. B. Howard, *Comb. Flame*, 119 (1999) 1-22
- [3] H. Richter, J. B. Howard, *Prog. energy combust. sci.*, 26 (2000) 565-608
- [4] H. Richter, O. A. Mazyar, R. Sumathi, W. H. Green, J. B. Howard, J. W. Bozzelli, *J. phys. chem. A*, 105 (2001) 1561-1573
- [5] H. Wang, M. Frenklach, *Comb. flame*, 110 (1997) 173-221
- [6] R. Wang, P. Cadman, *Comb. flame*, 112 (1998) 359-370
- [7] C. Descamps, G. L. Vignoles, O. Feron, F. Langlais, J. Lavenac, *J. Electrochem. Soc.*, 148 (2001) C695-C708
- [8] A. Becker, K. Hüttinger, *Carbon*, 36 (1998) 177-199
- [9] A. Becker, K. Hüttinger, *Carbon*, 36 (1998) 201-211
- [10] A. Becker, K. Hüttinger, *Carbon*, 36 (1998) 213-224
- [11] P. Barbé, Y. Li, P.M. Marquaire, G.M. Côme, F. Baronnet, *Oxid. Commun.*, 19 (1996) 173-185
- [12] D. Matras, J. Villermaux, *Chem. eng. Sci.*, 28 (1973) 129-137
- [13] M. Chambon, P.M. Marquaire, G.M. Côme, *C1. Mol. Chem.*, 2 (1987) 47-59
- [14] P.M. Marquaire, R. Wörner, P. Rambaud, F. Baronnet, *Organohalogen Compounds*, 40 (1999) 519
- [15] A. Becker, K. Hüttinger, *Carbon*, 36 (1998) 177-199
- [16] O. Feron, F. Langlais, R. Naslain, J. Thebault, *Carbon*, 37 (1999) 1343-1353
- [17] G.F. Glasier, P.D. Pacey, *Carbon*, 39 (2001) 15-23
- [18] I. Ziegler, R. Fournet, P. M. Marquaire, accepted for publication in *J Anal. Appl. Pyrolysis*, editor's code BM463
- [19] I. Ziegler, R. Fournet, P. M. Marquaire, accepted for publication in *J Anal. Appl. Pyrolysis*, editor's code BM468
- [20] I. Ziegler, R. Fournet, P. M. Marquaire, «*Pyrolysis of propane for CVI of pyrocarbon part II*», *J Anal. Appl. Pyrolysis*, submitted for publication
- [21] R. Fournet, J. C. Bauge, F. Battin-Leclerc, *Int. J. Chem. Kinet.*, 31 (1999) 361-379
- [22] I. Da Costa, R. Fournet, F. Billaud, F. Battin-Leclerc, *Int. J. Chem. Kinet.*, 35 (2003) 503-524
- [23] R. Bounaceur, I. Da Costa, R. Fournet, F. Billaud, F. Battin-Leclerc, *Int. J. Chem. Kinet.*, in press
- [24] W. Tsang, *J Phys Chem Ref Data*, 17 (1988)
- [25] P.A. Glaude, V. Warth, R. Fournet, F. Battin-Leclerc, G. Scacchi, G.M. Côme, *Int. J. Chem. Kin.*, 30 (1998) 949-959
- [26] D.L. Baulch, C.J. Cobos, R.A. Cox, P. Franck, G.D. Hayman, Th. Just, J.A. Kerr, T.P. Murrells, M.J. Pilling, J. Troe, R.W. Walker, J. Warnatz, *Combust Flame* 98 (1994) 59-79
- [27] W. Tsang, R.F. Hampson, *J Phys Chem Ref Data*, 15 (1986)
- [28] B. Heyberger, N. Belmekki, V. Conraud, P.A. Glaude, R. Fournet et F. Battin-Leclerc, *Int. J. Chem. Kin.*, 34 (2002) 666-677
- [29] P.R. Westmoreland, A.M. Dean, J.B. Howard, J.P. Longwell, *J. Phys. Chem.*, 93 (1989) 8171
- [30] R. Miller, C. Melius, *Combust Flame* 91 (1992) 21-39
- [31] S.E. Stein, J. A. Walker, M.M. Suryan, A. Fahr, *Int. Combust. Proc*, 23 (1990) 85
- [32] M. Weissman, S. W. Benson, *Prop. Energy Combust. Sci.*, 15 (1989) 273
- [33] N.M. Marinov, W.J. Pitz, C.K. Westbrook, M.J. Castaldi, S.M. Senkan., *Combust. Sci. Tech.*, 116-117 (1996) 211
- [34] V. Bloch-Michel, Ph. D. thesis, Institut National Polytechnique de Lorraine, Nancy, (1995)
- [35] J. Troe, *Ber. Bunsenges. Phys. Chem*, 78 (1974) 478
- [36] C. Muller, V. Michel, G. Scacchi, G.M. Côme, *J. Chim. Phys.*, 92 (1995) 1154
- [37] S.W. Benson, *Methods for the Estimation of Thermochemical data and Rate Parameters*, Wiley, New York, 1976
- [38] R.J. Kee, F.M. Rupley, J.A. Miller, Sandia Laboratories Report, SAND 89-8009B, 1993.
- [39] C. F. Melius, M. E. Colvin, N. M. Marinov, W. J. Pitz, S. M. Senkan. Twenty-sixth Symposium (International) on Combustion, The combustion Institute, Pittsburgh, 1996, p. 461-480