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2	Pyrolysis of <i>n</i>-Octane at Very Low Concentration and Low Temperature
3	
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13	Abstract
14	Hydrocarbon pyrolysis concerns many different fields (petroleum geochemistry, refinery, fuel
15	thermal stability, pyrocarbon deposition, etc.). It is therefore studied in a wide variety of
16	temperature-pressure experimental conditions, which strongly affect the chemistry of
17	hydrocarbons cracking.
18	An experimental study of the pyrolysis of <i>n</i> -octane has been performed at very low reactant
19	concentration (1 mbar diluted in inert gas - total pressure 1500 mbar - molar fraction 0.07%) in a
20	closed reactor, at temperatures ranging between 350°C and 450°C, and reaction time from 1 h to
21	70 h. The major products of the reaction are 1-alkenes (C_2H_4 to C_7H_{14}), methane and ethane;
22	other alkanes (C ₃ H ₈ to C ₆ H ₁₄) are minor products. At 450°C and 4 h, the conversion is close to
23	9% and we observe, in terms of molar fractions:
24	$C_2H_4 \! > \! C_3H_6 \! \approx CH_4 \! > \! C_4H_8 \! > \! C_5H_{10} \! > \! C_6H_{12} \! \approx C_2H_6 \! > \! C_7H_{14}$
25	These experimental results are very different from those of the thermal decomposition of n-

These experimental results are very different from those of the thermal decomposition of *n*alkanes at the same low temperature but at high pressure. In particular, the cracking stoichiometric equations (for example: $C_8H_{18} = C_6H_{14} + C_2H_4$) are not observed since alkanes (except methane and ethane) are in very low quantities. This can be explained by the very low concentration of reactant which limits the bimolecular reactions. In our conditions, the radicals decompose several times by beta-scissions of C-C bonds when it is possible (unimolecular reaction), rather than react by H-transfers (metathesis) with the reactant (bimolecular reaction) which produce alkanes. A detailed free radical mechanism (184 reactions, 16 molecules and 18 radicals – mechanism available as Supplementary Material) allows modelling the experimental results.

35

36 Keywords

37 Pyrolysis, *n*-Octane, Thermal decomposition, High dilution of reactant, Kinetic modelling.

38

39 **1. Introduction**

40 Thermal chemistry of hydrocarbons during pyrolysis is important in many research fields as 41 petroleum geochemistry [1-3], refining of crude oils, cracking of hydrocarbons to produce light olefins [4-7], thermal decomposition of endothermic jet fuels [8-10], conversion of coal and 42 43 biomass to liquid fuels [11-14], depolymerization and recycling of synthetic polymers [15-17], 44 pyrocarbon deposition for the elaboration of C/C composite materials [18-20], etc. The reaction 45 conditions considered cover a very wide range of time and temperature, from 150°C during several millions of years in geochemistry studies, to 900°C for a few milliseconds or seconds 46 47 during ethane/propane steam-cracking for instance. The pressure (and consequently the 48 concentration of hydrocarbons) can also vary in a very large domain, from some millibars to 49 1000 bar. This diversity of pyrolysis conditions is illustrated in different reviews (e.g. [21, 22]). Free-radical reaction pathways are considered as the dominant mechanisms for pyrolysis 50 51 reactions of organic materials (e.g. [22-24]). The pyrolysis chemistry of the same reactant (and 52 the main products formed) can largely be modified according to the conditions of the reaction (temperature, pressure and time). The knowledge of the thermal reaction mechanism and the rate 53

of the different pathways provide means to better understand hydrocarbon pyrolysis as well as
valuable information for kinetic modelling.

The study of the pyrolysis of *n*-alkanes is simpler than that of other hydrocarbons or organic 56 57 components. It is rather well known because it has been widely studied for a long time (e.g. [24-34]). Except for methane, the pyrolysis of alkanes consists of free-radical chain reactions. The 58 59 chemistry is similar whatever the size of the alkane, yet the number of products formed (and the 60 size of the reaction mechanism) increases with the number of carbon atoms of the molecule. At 61 low and usual pressure (0.1-10 bar), the pyrolysis of an alkane produces 1-alkenes and smaller 62 alkanes or hydrogen by cracking reaction. For example, the pyrolysis of propane leads to two 63 main stoichiometric equations:

$$C_3H_8 = C_2H_4 + CH_4$$

65
$$C_3H_8 = C_3H_6 + H_2$$

66 This reaction is used for olefin production by steam-cracking for instance.

In petroleum geochemistry, at high pressure (P>100bar) and low temperature (200<T<500°C), several alkanes were chosen as model molecules of the alkane family in oils. For instance, *n*hexane was chosen [28-29], as well as *n*-pentacosane [35], *n*-hexadecane [36-38] and *n*-octane [39]. In HP-LT (High Pressure-Low Temperature) conditions, the pyrolysis of alkanes is a long chain radical-reaction with two major types of propagation chains: a cracking chain and an alkylation one.

In HP-LT conditions, the detailed kinetic model of alkane pyrolysis was already investigated by several authors (e.g. [24, 29, 40-42]). Therefore, only the major aspects will be recalled here. The pyrolysis of an alkane (here called $\ll \mu H \gg [40]$) can be schematized by the following freeradical cracking mechanism where μ and β are free radicals.

Each cracking propagation chain includes two steps: a decomposition reaction by β-scission and
an H-transfer reaction:

80	Cracking chain: μ \rightarrow alkene + β .			
81	$\begin{cases} \beta \cdot + \mu H \longrightarrow alkane-minus + \mu \cdot \end{cases}$			
82	The corresponding cracking stoichiometric equation (I) is:			
83	$\mu H = alkane-minus + alkene$			
84	where β is a radical lighter than μ , and « alkane-minus » is an alkane lighter than the reactant			
85	μΗ.			
86	The alkylation propagation chains include two types of free radical reactions: additions of μ			
87	radicals to alkenes and H-transfers:			
88				
89	Alkylation chain: $\int \mu$ + alkene $\rightarrow \mu$ -alk-plus [.]			
90	μ -alk-plus·+ μ H \rightarrow alkane-plus + μ ·			
91				
92	It leads to the alkylation stoichiometric equation (II):			
93	alkene + μ H = alkane-plus			
94	where μ -alk-plus is a radical heavier than μ , and « alkane-plus » is the corresponding alkane			
95	which is heavier than the reactant μ H.			
96	At low temperature, the addition reactions are fast and the alkylation chains become important,			
97	because the activation energy of the additions is particularly low (about 25-34 kJ/mol). So the			
98	alkenes become minor products and the global (I + II) stoichiometric equation is:			
99	$\mu H + \mu H = alkane-minus + alkane-plus$			
100	Isomerization reactions also play an important role in product distribution. They can be			
101	unimolecular (1,4 and 1,5 H shift isomerization) and bimolecular by H-transfers between the			
102	reactant μH and one of its associated radicals μ_i leading to another isomer radical μ_j :			
103	μ_i \longrightarrow μ_j			
104	$\mu_i + \mu H \longrightarrow \mu_j + \mu H$			
105				

We already studied and modelled the pyrolysis at high pressure (700 bar) and low temperature $(300-400^{\circ}C)$ of *n*-octane [39] and hexadecane [36-38]. The mechanisms described above lead to modelling results consistent with the experimental ones and they are therefore considered as sufficiently complete (meaning that no major reaction was missing).

110 For *n*-octane pyrolysis, there are 4 radicals μ_i (i = 1 to 4, Figure 1) and 6 stoichiometric 111 equations. The major products are:

- 112 6 "alkane-minus": CH_4 to C_6H_{14}
- 113 6 "alkane-plus": C₁₀H₂₂ to C₁₅H₃₂

114 and the alkenes are minor products : C_2H_4 to C_7H_{14}

115 The objective of this work is to provide background information on the radical reactions 116 occurring during the pyrolysis of *n*-octane at very low reactant concentration (1 mbar diluted in 117 inert gas - total pressure 1500 mbar - molar fraction 0.07%). It is to be noted that the pressure 118 dependence of rate constant ("fall-off") [e.g. 23] is not studied here, because the total pressure is 119 always above 1 bar. These results are used for constructing a kinetic model. Conditions of low 120 reactant concentration (≤ 10 mbar of partial pressure) can be found in various processes or 121 natural conditions: unburned gas and pollutants in fumes [43, 44], low pressure plasmas, 122 chemical vapor deposition (CVD) [45-48], very low pressure pyrolysis (VLPP) studies [25-28], 123 atmospheric chemistry (earth or other planets) [49, 50], etc.

124

125 **2. Experimental technique**

The experimental pyrolysis study of *n*-octane has been performed in gas phase at very low reactant pressure (1 mbar) in a closed reactor (1 L) made of Pyrex. The *n*-octane is diluted in argon and the total pressure is close to 1500 mbar. Special care was taken to avoid oxygen traces. The temperatures range between 350°C and 450°C and the reaction time from 1 h to 70 h. The analysis was performed by two on-line gas chromatographs. Figure 2 shows the flow sheet of the experimental apparatus.

The experimental setup is connected to a vacuum pump ($< 10^{-3}$ mbar). The gases are introduced 132 133 in the reactor via a round-bottomed flask (2 L) which allows the mixing of the reactant and the 134 inert gas (argon). The liquid reactant (n-octane) is introduced by a syringe through a double 135 septum, protected from the air by a flow of argon. The amount of reactant is very small (10-50 136 μ L), as to ensure that it is totally vaporized in the mixer which is under vacuum (<10⁻³ mbar). 137 Inert gas is introduced by a central injector equipped with 4 nozzles in order to homogenize the 138 mixture. The total pressure in the mixer reaches 2-3 bar, which allows the expansion of the gas 139 toward the reactor in a second step.

140 The main three steps of an experiment are:

141 - pumping of all experimental setup and heating of the empty reactor,

142 - mixing of the reactant-argon mixture in the mixer and waiting for the homogenization
143 during 10 min,

- expansion of the gases toward the reactor and beginning of the thermal reaction.

During the same experiment, an aliquot fraction is removed at different reaction times from the reactor by expansion toward the heated analysis line. The amount of the aliquot fraction is very small and controlled by the pressure in the reactor (maximum drop of pressure = 20 mbar). The pressure drops are small in regards to the total pressure in the reactor (1500 mbar). Therefore, several aliquot fractions can be removed from the reactor without disturbing the reaction.

The analysis of the reactant and the products is performed by two online Gas Chromatographs. The chromatograph HEWLETT-PACKARD HP 6850 is equipped with a FID and a semicapillary column (GS-Alumina, length 30 m, diameter 0.53 mm). The temperature program of the oven is as follows: the initial temperature is set at 40°C during 10 min, then a heating rate of 10 °C/min is applied up to 190°C, and the final temperature is kept at 190°C during 20 min. This allows the analysis of the light alkanes and alkenes (from C₁ to C₈). In this setup, hydrogen cannot be measured.

157 The chromatograph SHIMADZU GC 17 is equipped with a FID and a packed column (Alltech,

length 3.6 m, stationary phase: 35% BCEF – 10% OV 101), which works isothermally at 50° C. It is particularly well adapted to the analysis of the heavy alkanes from C₉ to C₁₅, but none of them was detected in the entire study. The GC calibrations were performed by using several standard mixtures.

All data presented in this paper were generally verified by three or four sets of GC data. The repeatability for the molar fractions is usually less than 5% for the major products. The carbon balance is typically 1 ± 0.05 and the C/H ratio remains quite constant (between 0.40 and 0.44 at 400° C and between 0.44 and 0.47 at 450° C).

166 **3. Experimental results**

167 The major products obtained are methane, ethane and 1-alkenes (C_2H_4 to C_7H_{14}). Figures 3 show 168 the evolution of conversion versus reaction time at different temperatures.

169 At 450°C and 4 h, the *n*-octane conversion is greater than 8% and the three main reaction 170 products are ethylene, propene and methane, with molar fractions ranging in the following order:

 $171 C_2H_4 > C_3H_6 \cong CH_4$

172 followed by higher alkenes and ethane:

173
$$C_4H_8 > C_5H_{10} > C_6H_{12} \cong C_2H_6 > C_7H_{14}$$

174 The minor products observed are alkanes from C_3H_8 to C_7H_{16} .

The evolution of products versus reaction time will be detailed beneath in section 5 dedicated to the modeling. Figure 4 represents the global evolution of alkanes-minus and alkenes that are the two families of products.

It should be noted that these experimental results are very different from the thermal decomposition of *n*-alkanes at the same low temperature but at high pressure [39]. In particular, the cracking stoichiometric equations (for example: $C_8H_{18} = C_2H_4 + C_6H_{14}$) are not observed since C_3^+ alkanes are in very low quantities and the alkylation stoichiometric equation (for example: $C_8H_{18} + C_2H_4 = C_{10}H_{22}$) are negligible: alkenes are important and alkanes-plus (C_8^+) are not detected. The experimental results at 450°C are given in Table 1 and the details as
Supplementary Materials.

185

186 **4. Discussion: kinetic mechanism of** *n***-octane pyrolysis at very low concentration**

In comparison with the study of the pyrolysis of *n*-octane at 700 bar [39], the range of temperature is the same (350-450°C), but the reactant partial pressure (1 mbar) is very different, the initial concentration of reactant being lower by more than a factor of 10^5 . The very low concentration of reactant (called µH) minimizes the importance of the bimolecular reactions in the mechanism, in particular the H-transfer in the cracking propagation chain:

192

$$\begin{array}{cccc} 193 \\ 194 \end{array} \left\{ \begin{array}{ccc} \mu \cdot & \rightarrow & alkene + \beta \cdot & (decomposition by \beta \text{-scission}) \\ \beta \cdot + \mu H & \rightarrow & \beta H & + \mu \cdot & (H\text{-transfer}) \end{array} \right.$$

195

In our low concentration conditions, the radicals are decomposed by β -scission of C-C bonds as much as possible (unimolecular reaction), rather than reacting by H-transfer with the reactant (bimolecular reaction, which produces an alkane). The methyl and ethyl radicals cannot be decomposed by β -scission of C-C bonds, so they react by H-transfer with the reactant and produce methane or ethane and μ which is the chain carrier radical. At low temperature and low pressure, the cracking propagation chain becomes:

202

203
204
205
206

$$\begin{pmatrix}
\mu^{\cdot} \rightarrow \text{alkene-1} + \beta^{\cdot} \\
\beta^{\cdot} \rightarrow \text{alkene-2} + \beta^{\cdot} \\
\beta^{i^{\cdot}} \rightarrow \text{alkene-3} + \beta^{j^{\cdot}} \text{ and when } \beta^{j^{\cdot}} = \text{CH}_{3^{\cdot}} \text{ or } \text{C}_{2}\text{H}_{5^{\cdot}}, \\
\text{CH}_{3^{\cdot}} \text{ or } \text{C}_{2}\text{H}_{5^{\cdot}} + \mu\text{H} \rightarrow \text{CH}_{4} \text{ or } \text{C}_{2}\text{H}_{6} + \mu^{\cdot} \\
207$$

208 For the *n*-octane pyrolysis, there are 4 μ_i radicals (Figure 1), which lead to 4 cracking

209 propagation chains and 4 stoichiometric equations.

210 From μ_1 radical, the low pressure propagation chain is:

211
$$\mu_1 \rightarrow C_2H_4 + C_6H_{13}$$

212
$$C_6H_{13} \rightarrow C_2H_4 + C_4H_9$$

213
$$C_4H_9^{\cdot} \rightarrow C_2H_4 + C_2H_5^{\cdot}$$

214
$$C_2H_5 + C_8H_{18} \rightarrow C_2H_6 + \mu^{-}$$
 (all μ_i radicals, including μ_1)

215 The corresponding cracking stoichiometric equation is:

216
$$C_8H_{18} = 3 C_2H_4 + C_2H_6$$
 (I')

217 From μ_2 radical, an equivalent propagation chain leads to the stoichiometric equation:

218
$$C_8H_{18} = C_3H_6 + 2C_2H_4 + CH_4$$
 (II')

219 In the case of μ_3 , there are two possibilities of C-C bond scission:

$$220 \qquad \mu_3 \rightarrow C_7 H_{14} + C H_3$$

221 and $\mu_3 \rightarrow C_4H_8 + C_4H_9$

222 These chain reactions lead to the following stoichiometric equations:

223
$$C_8H_{18} = CH_4 + C_7H_{14}$$
 (III'a)

224 $C_8H_{18} = C_4H_8 + C_2H_4 + C_2H_6$ (III'b)

In the μ_4 radical, there are also two possibilities of C-C bond scission and the stoichiometric equations are:

227 $C_8H_{18} = C_6H_{12} + C_2H_6$ (IV'a)

228
$$C_8H_{18} = C_5H_{10} + C_2H_4 + CH_4$$
 (IV'b)

So, the stoichiometric equations lead to the formation of two alkanes, CH_4 and C_2H_6 , and all alkenes from C_2 to C_7 . This well agrees with the main products observed when the pyrolysis of *n*-octane is performed at very low reactant concentration.

232 If we suppose, in a first approximation, that all the cracking stoichiometric equations have the

233 same rate, the global stoichiometric equation is:

234 $6 C_8 H_{18} = 7 C_2 H_4 + 3 C H_4 + 3 C_2 H_6 + C_3 H_6 + C_4 H_8 + C_5 H_{10} + C_6 H_{12} + C_7 H_{14}$

- 235 That leads to the following classification:
- 236 $C_{2}H_{4} > CH_{4} = C_{2}H_{6} > C_{3}H_{6} = C_{4}H_{8} = C_{5}H_{10} = C_{6}H_{12} = C_{7}H_{14}$ (without alkanes in C₃₊)

The classification has to be compared with our experimental results at 450°C and 4 h (Figures 5 and 6):

239 $C_2H_4 > CH_4 \approx C_3H_6 > C_4H_8 > C_5H_{10} \approx C_6H_{12} > C_2H_6 > C_7H_{14} >> C_3H_8$, C_4H_{10} , C_5H_{12} , C_6H_{14} and

240 C₇H₁₆

The little quantitative differences between the experimental classification and the classification obtained by the stoichiometric equations could be explained by three approximations. First, the concentrations of the μ_i are not equal, because μ_1 is a primary radical which is less stable than a secondary one:

245
$$[\mu_1^{-1}] < [\mu_2^{-1}] \sim [\mu_3^{-1}] \sim [\mu_4^{-1}]$$

246 Consequently, the stoichiometric equation I' (leading to C_2H_6) is overestimated in the argument 247 which only considers the stoichiometric equations.

248 Another correction is that the decompositions by β -scission of C-H bonds are not completely 249 negligible at 450°C. They lead to the conversion of ethane into ethylene, which is the major 250 product:

 $251 \qquad C_2H_5 \rightarrow C_2H_4 + H^{\cdot}$

252 $H' + C_8 H_{18} \rightarrow H_2 + \mu'$

Finally, the formation of C_3^+ alkanes in very low quantities indicates that the H transfer reactions of β -radicals (C_3 - C_6 radicals) are not totally negligible and produce C_3^+ alkanes:

255
$$\beta \cdot + \mu H \rightarrow C_{3+} alkanes + \mu \cdot$$

This brief kinetic interpretation well explains the chemistry observed for the *n*-octane pyrolysis at low reactant concentration and low temperature, and the differences in the product distribution obtained at high concentration and pressure (competition: unimolecular versus bimolecular reactions).

261 **5. Modeling of** *n***-octane thermal decomposition at very low reactant concentration.**

On the basis of these free-radical reactions, a systematic approach is used to build a detailed mechanism of *n*-octane pyrolysis at low reactant concentration and low temperature. Using EXGAS software [40, 51], the mechanism (primary and partial secondary) is made of 184 reactions involving 34 species (16 molecules and 18 radicals). The kinetic data originate from NIST Database [52] or literature and are summarized in [40]. The simulations are performed using Chemkin II software [53], in a closed isochoric and isothermal reactor (Senkin).

The comparison between the experimental results and simulation ones led to the adjustment of some rate constants by a minor factor (less or equal to 10) in order to better account for main pyrolysis products. Figures 5, 6 and 7 present the comparison between the experimental data and the simulation results of the molar fractions (*n*-octane and reaction products) versus time (1 to 240 minutes) at 450°C and 1 mbar of *n*-octane partial pressure (total pressure 1500 mbar - molar fraction 0.07%).

274 The detailed kinetic model accounts for the nature of the products observed as well as for their 275 amounts, at least semi-quantitatively. The evolution of alkenes, n-octane and propane is well 276 simulated by the kinetic model, although ethene is very slightly over-estimated, and pentene and 277 hexene are under-estimated, but they are minor products. The overestimation of ethene can be 278 due to additions of some radicals to alkenes, which are secondary reactions not taken into 279 account by the model. Methane and ethane are also very slightly overestimated by the model, 280 probably for the same reason, because methyl and ethyl radicals are the predominant radicals. In 281 the case of ethane, this may also be due to the decomposition of C-H bonds, which is not 282 completely negligible at 450°C and leads to the conversion of ethane into ethylene. Nevertheless 283 we can therefore conclude that the kinetic model is globally validated as well as the kinetic 284 scheme proposed to explain the chemistry observed at very low concentration.

By simulation of the kinetic model, the chain length can be estimated by the ratio of the global propagation rate to the initiation rate. The main H-transfers with *n*-octane are those implying the

methyl and ethyl radicals. The chain length is equal to 120 at 450° C and low *n*-octane concentration (molar fraction 0.07%). The chain length increases when the temperature decreases and in our conditions, the chain length is always very high.

When a reaction follows a first order kinetic law, the plot of log (1-conversion) versus time must give a linear relationship and the slope corresponds to the rate constant. Assuming a first order kinetics, we can estimate the apparent activation energy of *n*-octane pyrolysis: it is close to 218 kJ/mol and the frequency factor is about 3.63×10^{10} (s⁻¹), in the range 350° C – 450° C and 1 mbar of *n*-octane partial pressure. This apparent activation energy is lower than that of alkane pyrolysis at the same temperatures but at high pressure (100-700 bar), which is close to 284-289 kJ/mol [35, 39, 42, 54].

This difference can be explained by the concentration of reactant that is totally different in our case in comparison to those applied in [35, 39, 42]. The elementary reactions that are important, are also different, depending on the reaction conditions. Indeed, in the chain propagation, the Htransfers of radicals with reactant, which produce smaller alkanes than the reactant, are in competition with the decomposition of this radical by β -scission which produce smaller alkenes:

302 β · \rightarrow alkene + β '· 303 β · + μ H \rightarrow alkane β H + μ ·

At very low reactant concentration, unimolecular decomposition reactions are greatly favoredover bimolecular reactions, and that leads to very different apparent activation energies.

306

307 6. Conclusion

An experimental study of the pyrolysis of *n*-octane has been performed at very low reactant concentration (1 mbar diluted in inert gas - total pressure 1500 mbar - molar fraction 0.07%) in a closed reactor, at temperatures between 350°C and 450°C and reaction time from 1 h to 70 h. The major products of the reaction are 1-alkenes (C_2H_4 to C_7H_{14}), methane and ethane. These experimental results are different from the thermal decomposition of *n*-octane at the same low

313	temperature but at high pressure (the major products are only alkanes at 700 bar).
314	Indeed, at very low reactant concentration, unimolecular decomposition reactions are greatly
315	favored over bimolecular reactions. In our low concentration conditions, radicals decompose
316	several times by β -scission of C-C bonds as much as possible (unimolecular reaction), rather
317	than react by H-transfer with the reactant (bimolecular reaction) which produces an alkane. The
318	methyl and ethyl radicals cannot decompose by C-C β -scission, and so they react by H-transfer
319	with the reactant and produce methane or ethane and μ , which is the chain carrier radical.
320	
321	On the basis of these free-radical reactions, a detailed kinetic model (184 reactions, 16 molecules
322	and 18 radicals) is proposed, which allows a satisfying description of the experimental results:
323	- the nature of the principal reaction products is correct,
324	- C ₂ H ₄ is the most important product,
325	- CH ₄ and C ₂ H ₆ are the only two important alkanes,
326	- the alkenes from C ₃ to C ₇ are formed in rather close quantities,
327	- the C_3^+ alkanes are very minor products.
328	These results of <i>n</i> -octane pyrolysis obtained at very low reactant concentration underline the
329	crucial role of concentration and partial pressure in the reaction pathways and products of the
330	alkane pyrolysis. They clearly demonstrate that results obtained at low partial pressure cannot be
331	extrapolated at high pressure and vice versa.
332	

- 335
- 336 [1] M. Vandenbroucke, F.Behar, J.L. Rudkiewicz, Kinetic modelling of petroleum formation and
- 337 cracking: implications from the high pressure/high temperature Elgin Field (UK, North Sea),
- 338 Org. Geochem. 30 (9) (1999) 1105–1125.
- 339 [2] K.E. Peters, M.G. Fowler, Applications of petroleum geochemistry to exploration and
- 340 reservoir management, Org. Geochem. 33 (1) (2002) 5–36.
- 341 [3] R.J. Hill, Y. Tang, I.R. Kaplan, Insights into oil cracking based on laboratory experiments,
- 342 Org. Geochem. 34 (12) (2003) 1651-1672.
- 343 [4] M. Bajus, V.C. Vesela, P.A. Leclercq, J.A. Rijks, Steam Cracking of Hydrocarbons. 2.
- 344 Pyrolysis of Methylcyclohexane, Ind. Eng. Chem. Prod. Res. Dev 18 (1) (1979) 135-142.
- 345 [5] G.F. Froment, Kinetics and reactor design in the thermal cracking for olefins production,
 346 Chem. Eng. Sci. 47 (9-11) (1992) 2163–2177.
- 347 [6] S.M. Sadrameli, A.E.S. Green, Systematics and modeling representations of naphtha thermal
- 348 cracking for olefin production, J. Anal. Appl. Pyrolysis, 73 (2) (2005) 305–313.
- 349 [7] K. M. Van Geem, D. Hudebine, M.F. Reyniers, F.Wahl, J. Verstraete, G. B. Marin,
- 350 Molecular reconstruction of naphtha steam cracking feedstocks based on commercial indices,
- 351 Comput. Chem. Eng., 31 (9) (2007) 1020–1034.
- 352 [8] T. Edwards, Cracking and deposition behavior of supercritical hydrocarbon aviation fuels,
- 353 Combust. Sci. Tech., 178 (1-3) (2006) 307–334.
- 354 [9] O. Herbinet, B. Sirjean, R. Bounaceur, R. Fournet, F. Battin-Leclerc, G. Scacchi, P.M.
- 355 Marquaire, Primary reactions of the thermal decomposition of tricyclodecane, J. Phys. Chem. A,
- 356 110 (39) (2006) 11298-11314.
- 357 [10] N. Vandewiele, G. Magoon, K. Van Geem, M.F. Reyniers, W. Green, G. Marin, Kinetic
- 358 Modeling of Jet Propellant-10 Pyrolysis, Energy Fuels, 29 (1) (2015) 413–427.
- 359 [11] P.R. Solomon, M.A. Serio, G.V., Despande, E. Kroo, Cross-linking reactions during coal

- 360 conversion, Energy Fuels 4 (1) (1990) 42–54.
- [12] S. Wang, H. Huang, K. Wang, M.T. Klein, W.H. Calkins, Kinetics of Coal Liquefaction
 Distillation Resid Conversion, Energy Fuels, 12 (6) (1998) 1335–1341.
- 363 [13] N. Howaniec, A. Smoliński, Effect of fuel blend composition on the efficiency of hydrogen-
- rich gas production in co-gasification of coal and biomass, Fuel 128 (2014) 442-450.
- 365 [14] J.G. Speight, Coal gasification processes for synthetic liquid fuel production, in: R. Luque,
- 366 J. Speight (Eds.), Gasification for Synthetic Fuel Production Fundamentals, Processes and
- 367 Applications, Woodhead Publishing Series in Energy, Elsevier Ltd, 2015.
- 368 [15] W. Kaminsky, B. Schlesselmann, C. Simon, Olefins from polyolefins and mixed plastics by
- 369 pyrolysis, J. Anal. Appl. Pyrol. 32 (1995) 19–27.
- [16] A. Uddin, K. Koizumi, K. Murata, Y. Sakata, Thermal and catalytic degradation of
 structurally different types of polyethylene into fuel oil, Polym. Degrad. Stab. 56 (1) (1997) 37–
 44.
- 373 [17] E. Hajekova, M. Bajus, Recycling of low-density polyethylene and polypropylene via
 374 copyrolysis of polyalkene oil/waxes with naphtha: product distribution and coke formation, J.
- 375 Anal. Appl. Pyrolysis 74 (1-2) (2005) 270–281.
- 376 [18] I. Ziegler, R. Fournet, P.M.Marquaire, Pyrolysis of propane for CVI of pyrocarbon part I:
- 377 Experimental and modeling study of the formation of toluene and aliphatic species, J. Anal.
- 378 Appl. Pyrol. 73(2) (2005) 212-230.
- 379 [19] I. Ziegler, R. Fournet, P.M. Marquaire, Pyrolysis of propane for CVI of pyrocarbon part II:
- 380 Experimental and modeling study of polyaromatic species, J. Anal. Appl. Pyrol. 73(2) (2005)381 231-247.
- [20] R. Lacroix, R. Fournet, I. Ziegler-Devin, P.M. Marquaire, Kinetic Modeling of Surface
 Reactions Involved in CVI of Pyrocarbon obtained by propane pyrolysis, Carbon 48 (1)
 (2010)132-144.
- 385 [21] S. Moldoveanu, Pyrolysis of organic molecules-Applications to Health and Environmental

- 386 Issues, first ed., Elsevier, 2009.
- 387 [22] P.E. Savage, Mechanisms and kinetics models for hydrocarbon pyrolysis, J. Anal. Appl.
 388 Pyrolysis 54 (1-2) (2000) 109–126.
- 389 [23] K.J. Laidler, L.F Louks, Comprehensive Chemical Kinetics, vol 5, Elsevier, 1972.
- 390 [24] M.L. Poutsma, Fundamental reactions of free radicals relevant to pyrolysis reactions, J.
- 391 Anal. Appl. Pyrolysis 54 (1-2) (2000) 5–35.
- 392 [25] F. O. Rice, K. F. Herzfeld, The Thermal Decomposition of Organic Compounds from the
- 393 Standpoint of Free Radicals. VI. The Mechanism of Some Chain Reactions, J. Am. Chem. Soc.,
 394 56 (1934) 284-289.
- 395 [26] D.L.Allara, R. Shaw, A compilation ok kinetic-parameters for the thermal degradation of
- 396 normal-alkane molecules, J. Phys. Chem. Ref. Data, 9 (3) (1980) 523-559.
- 397 [27] T. J. Ford, Liquid-Phase Thermal Decomposition of Hexadecane: Reaction Mechanisms,
- 398 Ind. Eng. Chem. Fundam., 25 (2) (1986) 240-243.
- 399 [28] F. Dominé, Kinetics of hexane pyrolysis at very high pressures. 1. Experimental study,
- 400 Energy Fuels 3 (1) (1989) 89–96.
- 401 [29] F. Dominé, P.M. Marquaire, C. Muller, G.-M. Côme, Kinetics of hexane pyrolysis at very
- 402 high pressures. 2. Computer modeling, Energy Fuels 4(1) (1990) 2–10.
- 403 [30] F. Khorasheh, M. R. Gray, High-Pressure Thermal Cracking of *n*-Hexadecane, Ind. Eng.
- 404 Chem. Res., 32 (9) (1993) 1853-1863.
- 405 [31] K.J. Jackson, A.K. Burnham, R.L. Braun, K.G. Knauss, Temperature and pressure
- 406 dependence of n-hexadecane cracking, Org. Geochem. 23 (10) (1995) 941–953.
- 407 [32] O. Herbinet, PM. Marquaire, F. Battin-Leclerc, R. Fournet, Thermal stability of *n*-dodecane:
- 408 experiments and kinetic modeling, J. Anal. Appl. Pyrol., 78(2) (2007) 419-429.
- 409 [33] M. J. De Witt, D. J. Dooling, L J. Broadbelt, Computer Generation of Reaction Mechanisms
- 410 Using Quantitative Rate Information: Application to Long-Chain Hydrocarbon Pyrolysis, Ind.
- 411 Eng. Chem. Res. 39 (2000) 2228-2237.

- 412 [34] J. Yu, S. Eser, Kinetics of Supercritical-Phase Thermal Decomposition of C10–C14 Normal
- 413 Alkanes and Their Mixtures Ind. Eng. Chem. Res. 36 (3) (1997) 585–591.
- 414 [35] F. Behar, M. Vandenbroucke, Experimental Determination of the Rate Constants of the *n*-
- 415 C25 Thermal Cracking at 120, 400, and 800 bar: Implications for High-Pressure/High416 Temperature Prospects, Energy Fuels 10 (4) (1996) 932-940.
- 417 [36] R. Bounaceur, G. Scacchi, P.M. Marquaire, F. Dominé, D. Dessort, B. Pradier, Inhibiting
- 418 effect of tetralin on the pyrolytic decomposition of hexadecane. Comparison with toluene, Ind.
- 419 Eng. Chem. Res. 41 (19) (2002) 4689–4701.
- 420 [37] V. Burklé-Vitzthum, R. Michels, G. Scacchi, P.M. Marquaire, D. Dessort, B. Pradier, O.
- 421 Brevart, Kinetic effect of alkylaromatics on the thermal stability of hydrocarbons under 422 geological conditions, Org. Geochem. 35 (1) (2004) 3-31.
- [38] V. Burklé-Vitzthum, R. Michels, R. Bounaceur, P.M. Marquaire, G. Scacchi, Experimental
 study and modeling of the role of hydronaphthalenics on the thermal stability of hydrocarbons at
- 425 laboratory and geological conditions, Ind. Eng. Chem. Res. 44 (24) (2005) 8972-8987.
- 426 [39] F. Lannuzel, R. Bounaceur, R. Michels, G. Scacchi, P.M. Marquaire, Reassessment of the
- 427 kinetic influence of toluene on *n*-alkanes pyrolysis, Energy Fuels 24 (7) (2010) 3817-3830.
- 428 [40] R. Bounaceur, V. Warth, P. M. Marquaire, G. Scacchi, F. Dominé, D. Dessort, B. Pradier,
- 429 O. Brevart, Modeling of hydrocarbons pyrolysis at low temperature. Automatic generation of
- 430 free radicals mechanisms, J. Anal. Appl. Pyrolysis 64 (2002) 103-122.
- 431 [41] F. Dominé, R. Bounaceur, G. Scacchi, P.M. Marquaire, D. Dessort, B. Pradier, O. Brévart,
- 432 Up to what temperature is petroleum stable ? New insights from a 5200 free radical reactions
- 433 model, Org. Geochem. 33 (12) (2002) 1487-1499.
- 434 [42] V. Burklé-Vitzthum, R. Bounaceur, P-M. Marquaire, F. Montel, L. Fusetti, Thermal
- 435 evolution of *n* and iso-alkanes in oils Part 1: Pyrolysis model for a mixture of 78 alkanes (C1-
- 436 C32) including 13,206 free radical reactions, Org. Geochem. 42 (5) (2011) 439-450.
- 437 [43] I. Ziegler-Devin, R. Bounaceur, C. Perrin, R. Wörner, F. Patisson, P. M. Marquaire, Kinetic

- 438 study of abatement of low concentration of dibenzofuran by oxidation Effects of co-reactants,
- 439 Chem. Eng. J. 218 (2013) 154-163.
- 440 [44] A. Tritz, I. Ziegler-Devin, C. Perrin, P.M. Marquaire, Experimental study of the oxidation
- 441 and pyrolysis of dibenzofuran at very low concentration, J. Env. Chem. Eng., 2 (2014) 143-153.
- 442 [45] G. Vignoles, F. Langlais, C. Descamps, A. Mouchon, H. Le Poche H, N. Reuge, CVD and
- 443 CVI of pyrocarbon from various precursors, Surf. Coat. Technol. 188-189 (2004) 241–249.
- 444 [46] K. Norinaga, O. Deutschmann, Detailed kinetic modeling of gas-phase reactions in the
- chemical vapor deposit of carbon from light hydrocarbons, Ind. Eng. Chem. Res. 46 (11) (2007)
 3547–3557.
- 447 [47] M. Frenklach, H. Wang, Detailed surface and gas-phase chemical kinetics of diamond
- 448 deposit, Phys. Rev. B: Condens. Matter, 43 (2) (1991) 1520-1545.
- [48] S.W. Benson, G. N. Spokes, Very Low Pressure Pyrolysis. III t-butyl hydroperoxide in
 Fused Silica and Stainless Steel Reactors, J. Phys. Chem. 72 (1968)1182-1186.
- [49] R. Atkinson, J. Arey, S. M. Aschmann Atmospheric chemistry of alkanes: Review and
 recent developments Atmospheric Environment, 42 (2008) 5859-5871
- [50] O. Venot, E. Hébrard, M. Agúndez, L. Decin, R. Bounaceur A new chemical scheme to
 study carbon-rich exoplanet atmospheres Astronomy & Astrophysics, in press 2015
 (arXiv:1502.03567)
- 456 [51] F. Battin-Leclerc, J. Biet, R. Bounaceur, G.M. Côme, R. Fournet, P.-A. Glaude, X.
- 457 Grandmougin, O. Herbinet, G. Scacchi, V. Warth, EXGAS-ALKANES-ESTERS: A software for
- the automatic generation of mechanisms for the oxidation of alkanes and esters, (2010) LRGP,
 UPR CNRS 3349
- 460 [52] J. A. Manion, R. E. Huie, R. D. Levin, D. R. Burgess Jr., V. L. Orkin, W. Tsang, W. S.
- 461 McGivern, J. W. Hudgens, V. D. Knyazev, D. B. Atkinson, E. Chai, A. M. Tereza, C.-Y. Lin, T.
- 462 C. Allison, W. G. Mallard, F. Westley, J. T. Herron, R. F. Hampson, D. H. Frizzell, NIST
- 463 Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version),

- 464 Release 1.4.3, Data version 2008.12, National Institute of Standards and Technology,
- 465 Gaithersburg, Maryland, 20899-8320. http://kinetics.nist.gov
- 466 [53] R.J Kee, F.M. Rupley, J.A. Miller, Chemkin-II: A Fortran chemical kinetics package for the
- 467 analysis of gas-phase chemical kinetics, (1989) Sandia National Laboratories, Livermore, CA.
- 468 [54] F. Behar, F. Lorant, L. Mazeas, Elaboration of a new compositional kinetic schema for oil
- 469 cracking, Org. Geochem. 39 (6) (2008) 764–782.
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474 TABLE CAPTION

- **Table 1:** Product distribution in mol. % Octane pyrolysis at 450°C-initial pressure of octane =
- 477 1 mbar total pressure = 1500mbar

CH4	-	9.40×10 ⁻⁴	1.39×10 ⁻³	1.87×10^{-3}	2.25×10 ⁻³
C ₂ H ₆	-	2.40×10 ⁻⁴	3.21×10 ⁻⁴	4.06×10 ⁻⁴	5.32×10 ⁻⁴
C3H8	-	8.07×10 ⁻⁶	1.01×10 ⁻⁵	9.46×10 ⁻⁶	1.31×10 ⁻⁵
C4H10	-	3.23×10 ⁻⁶	4.90×10 ⁻⁶	4.71×10 ⁻⁶	5.27×10 ⁻⁶
C ₂ H ₄	-	3.28×10 ⁻³	4.79×10 ⁻³	6.31×10 ⁻³	7.56×10 ⁻³
C3H6	-	1.32×10 ⁻³	1.94×10 ⁻³	2.65×10 ⁻³	3.22×10 ⁻³
C4H8	-	6.56×10 ⁻⁴	8.85×10 ⁻⁴	1.16×10 ⁻³	1.40×10 ⁻³
C5H10	-	5.18×10 ⁻⁴	7.50×10 ⁻⁴	8.74×10 ⁻⁴	9.61×10 ⁻⁴
C ₆ H ₁₂	-	4.94×10 ⁻⁴	6.43×10 ⁻⁴	7.50×10 ⁻⁴	8.60×10 ⁻⁴
C7H14	-	1.02×10^{-4}	1.43×10 ⁻⁴	2.16×10 ⁻⁴	2.02×10 ⁻⁴
C8H18	6.65×10 ⁻²	6.49×10 ⁻²	6.31×10 ⁻²	6.21×10 ⁻²	6.11×10 ⁻²











Figure 4. Comparison between experimental (dots) and simulation (solid lines) molar fractions
of the alkanes-minus and alkenes, as a function of time, at 450°C and 1mbar initial *n*-octane
pressure.



Figures 5. Comparison between experimental (dots) and simulation (solid lines) molar fractions
of the alkenes (from ethylene to heptene), as a function of time, at 450°C and 1mbar initial *n*octane pressure.





Figures 6. Comparison between experimental (dots) and simulation (solid lines) molar fractions
of the alkanes (from methane to butane), as a function of time, at 450°C and 1mbar initial *n*octane pressure.



534	Figure 7. Comparison between experimental and simulation molar fraction of <i>n</i> -octane, as a
535	function of time, at 450°C and 1mbar initial <i>n</i> -octane pressure.