

## MECHANISTIC MODELLING OF THE PYROLYSIS OF 3-METHYLPENTANE

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### ABSTRACT

A mechanistic model of the thermal decomposition reactions of 3-methylpentane at low conversion (< 5%) using as a basis a complex free-radical chain mechanism has been adjusted and compared to the observed product distribution. A reasonably good agreement between the computed curves and the experimental results obtained from an earlier work has been obtained.

Even at low conversion, the secondary reactions of olefinic primary products satisfactorily account for the self-inhibition of 3-methylpentane pyrolysis.

### INTRODUCTION

The thermal reactions of hydrocarbons in the gas phase are of fundamental and economic importance in many industrial processes such as pyrolysis, oxidation and chlorination. The understanding of the corresponding reaction mechanism is a further step towards the improvement of product yields, a lower energy consumption and a better selectivity. A better description of the different stages of a reaction leads to an increase in the number of elementary steps and enables quite complex reaction mechanisms to be written.

The development of improved numerical techniques for solving the set of differential equations which are derived from the reaction schemes has led to their increasing exploitation in the analysis and investigation of complex kinetic systems.

Various programs such as CHEMKIN [1], NASAKIN [2] and MORSE [3] have been used in the present work in which we have chosen, as a first example, the thermal decomposition of 3-methylpentane.

This reaction has been previously investigated in a conventional static apparatus at 420 °C and 133 mbar [4]. This experimental study was developed as a first step towards a more detailed understanding of the basic

phenomena involved during the thermal cracking of hydrocarbons, more particularly the influence of the structure (linear or branched-chain) on the yields of ethylene.

Our investigations on the pyrolysis of alkanes are a part of a larger project in which the experimental results will be subsequently used as a reference for the studies of co-reactions between an alkane and a gas-oil component.

In the present paper, we describe a further step; taking into account the previous experimental results, we perform computer simulations of 3-methylpentane pyrolysis using the MORSE package in order to determine the yields of products versus residence times, using the assessed values of the rate constants for the elementary reactions of this pyrolysis.

## KINETIC MODEL

A detailed investigation of a chemical reaction requires the writing of a reaction mechanism which accounts for the different steps of the reaction. A reaction mechanism is based on  $s$  elementary steps involving  $c$  components (reactants and products). An elementary step describes the chemical act at the molecular level. A termolecular reaction (involving three species, molecules and radicals) is not common; most elementary steps are unimolecular or bimolecular.

The reaction mechanism can be written as

$$\sum_{j=1}^c \nu_{ij} C_j = 0; \quad i = 1, 2, \dots, s, \quad \nu_{ij} > 0 \text{ (product)}, \quad \nu_{ij} < 0 \text{ (reactant)} \quad (1)$$

For each reaction,  $i$ , the reaction rate is

$$r_{ij} = k_i \prod_{j=1}^c C_{ij}^{(|\nu_{ij}| - \nu_{ij})/2} \quad (2)$$

$k_i$  is defined by the Arrhenius law

$$k_i = A_i \exp(-E_i/RT) \quad (3)$$

Knowing the rate constant  $k_i$  of an elementary step, we can deduce the reverse constant  $k_{-i}$  from the relationship

$$k_{-i} = k_i / K_{C_i} \quad (4)$$

with  $K_{C_i}$  being the equilibrium constant.

$$K_{C_i} = K_{p_i} (P_{\text{atm}}/RT)^{\sum_{j=1}^c \nu_{ij}} \quad (5)$$

and

$$K_{p_i} = \exp[(\Delta S_i^\ominus/R) - (\Delta H_i^\ominus/RT)] \quad (6)$$

which can be calculated from the thermodynamic relationships

$$\Delta S_i^\ominus/R = \sum_{j=1}^C \nu_{ij} (S_j^\ominus/R) \quad (7)$$

and

$$\Delta H_i^\ominus/R = \sum_{j=1}^C \nu_{ij} (\Delta H_{fj}^\ominus/RT) \quad (8)$$

If we know all the elementary rates  $r_i$  the overall rate of formation of a component  $C_j$  is

$$R_j = \sum_{i=1}^s \nu_{ij} r_i \quad (9)$$

Such a relationship holds for all components ( $j = 1, 2, \dots, c$ ).

To calculate the concentrations at the outlet of an ideal reactor, we have to solve either a system of differential equations with initial conditions or a system of algebraic equations.

The simulation of a complex chemical reaction system requires special numerical methods because of the 'stiffness' of the system of equations. The 'stiffness' is defined by

$$S = \frac{\text{Max}_\lambda (\text{Re}(-\lambda))}{\text{Min}_\lambda (\text{Re}(-\lambda))} \quad (10)$$

where  $\lambda$  are the eigenvalues associated to the Jacobian matrix corresponding to the system of equations.

For stiff systems, this ratio is larger than  $10^3$ . In our example, the value is approximately  $10^6$ – $10^8$ ; this is common in mechanisms involving chain mechanisms and is caused by the wide range spanned by the rates of the elementary reactions.

Standard numerical techniques are the Newton method for non-linear algebraic systems and the Runge-Kutta method for non-linear differential systems. Classical methods usually require excessive computer time which can be greatly reduced by including facilities for varying the step-size and for linking it to an estimate of the overall error.

In what follows, we briefly describe the MORSE computer program which allows the simulation to be performed.

## SOFTWARE CHARACTERISTICS

The general structure of the computer program used in the present work is shown in Fig. 1.

The input of the reaction mechanism and of the Arrhenius parameters is achieved by means of a very simple linear notation [5]. For example, the

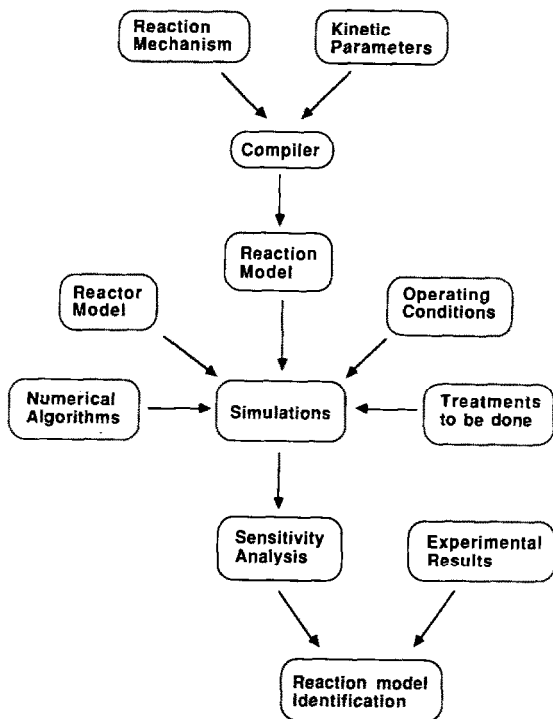


Fig. 1. Structure of the computer program.

breaking of a C–C bond in a 3-methylpentane molecule (initiation step) is written as



$$\text{AD} = 6.3 \times 10^{16}$$

$$\text{ED} = 79.2 \times 10^3$$

where / represents a covalent bond, AD is the pre-exponential factor and ED is the activation energy in  $\text{cal mol}^{-1}$ .

Setting up the mathematical model of the reaction is achieved by a specific compiler named COMPIL [6] which numbers the components and the reactions, determines the matrix of the stoichiometric coefficients, builds up the tables of kinetic parameters and finally encodes the rate constant as a function of temperature.

The specifications of the particular problem to be dealt with are then introduced into the computer by the unit DON.

This program creates a data repertory (operating conditions, type of reactor, etc) necessary for the simulation. It also permits in an optional way, the specification of the type of treatment: (a) a reaction simulation which calculates the concentration of the various components at the outlet; (b) a sensitivity analysis to determine the negligible, determining and non-de-

termining reactions, in order to reduce the size of the reaction mechanism; or (c) facilities for modifying the initial reaction mechanism (rate constants, elementary steps, step-size of the integration technique, etc).

Using the reaction mechanism written by the compiler and the data repertory, the SIMVIS program simulates the reaction and performs the additional requirements. This program was designed to perform the calculations of reactions in the gas phase for continuous-flow stirred tank reactor (CFSTR). The computations for a plug-flow reactor (PFR) can be achieved by treating the PFR as a series of CFSTRs. The batch reactor (conventional static system) is equivalent to a PFR in which the reaction time is equal to the PFR residence time when the gas flow rate does not change.

Using the previous symbols, the mass balance for the  $j$ th component in a CFSTR can be written

$$F_{j0} + R_j V = F_j \quad (11)$$

$$C_{j0} Q_0 + R_j V = Q C_j \quad (12)$$

where  $C_j$  is the concentration of the  $j$ th species,  $F_j$  is the molar flow rate of the  $j$ th species,  $Q$  the gas flow rate and  $V$  the reactor volume, with

$$R_j = \sum_{i=1}^s \nu_{ij} r_i \quad (13)$$

$$C_j = (C_{j0} + \tau R_j) / (Q/Q_0) \quad (14)$$

where  $\tau = V/Q_0$ , is the space time. We have also

$$Q_0 = \sum_{j=1}^c F_{j0} V_{j0} \quad (15)$$

and

$$Q = \sum_{j=1}^c F_j V_j \quad (16)$$

where  $V_j$  and  $V_{j0}$  are the partial molar volumes of component  $j$ . Taking eqn. (11) into account

$$Q = \sum_{j=1}^c (F_{j0} + R_j V) V_j \quad (17)$$

For gaseous species in an isothermal reactor, we can write

$$Q = \sum_{j=1}^c F_{j0} V_j + \sum_{j=1}^c R_j V V_j \approx \sum_{j=1}^c F_{j0} V_{j0} + \sum_{j=1}^c R_j V V_j \quad (18)$$

with

$$V_j = V_{j0} = RT/P \quad (19)$$

and

$$Q = Q_0 + (RTV/P) \sum_{j=1}^c R_j \quad (20)$$

Whence

$$Q = Q_0 = (RTV/P) \sum_{j=1}^c R_j \quad (21)$$

and

$$Q/Q_0 = 1 + \tau(RT/P) \sum_{j=1}^c R_j \quad (22)$$

Finally, we obtain a non-linear system of  $c$  equations in the  $c$  unknowns,  $C_j$ . The solutions of this system is obtained by the Newton method. The  $f$  function is defined by

$$f(C_j) = C_j - (C_{j0} + \tau R_j)/(Q/Q_0) \quad (23)$$

The values of  $C_j$  should be such that  $f(C_j) = 0$  for  $j = 1, \dots, C$ . If we linearise the  $f$  function near an initial approximation,  $C_j^k$ , of the solution, we have

$$f(C_j^{(k+1)}) \approx f(C_j^{(k)}) + (\partial f/\partial C_j)_{C_j^{(k)}} (C_j^{(k+1)} - C_j^{(k)}) \approx 0; \quad k = 0, 1, 2 \dots \quad (24)$$

which allows the following approximation  $C_j^{(k+1)}$  to be obtained by solving the system

$$f(C_j^{(k)}) + (\partial f/\partial C_j)_{C_j^{(k)}} (C_j^{(k+1)} - C_j^{(k)}) = 0 \quad (25)$$

This type of iteration is continued until we obtain a stable value of the concentration.

## INITIAL SIMULATION AND SENSITIVITY ANALYSIS

The reaction mechanism is introduced in the computer taking into account the criteria required by the MORSE program. After compilation of this input, a first simulation, in our experimental conditions, permits the concentration  $C_j$  of each component to be obtained.

Taking into account the complexity of the reaction and for a better understanding of the phenomena, we investigate, as a first stage, only the primary mechanism. The experiments and simulation were performed at small extents of reaction ( $< 5\%$ ).

Care was taken to ensure that the discretisation error is small, by optimising the number of CFSTRs and also by comparing our results with those obtained by means of the LSODE package [1].

### Sensitivity analysis

The calculation of the sensitivity coefficients,  $\sigma_{ij} = (\Delta C_j / C_j) / (\Delta k_i / k_i)$ , corresponding to the formation of a product  $j$  ( $C_j$  is the concentration of  $j$ ) from an elementary step  $i$  allows the list of determining elementary steps which can have an influence on the value of  $C_j$  to be known. They are therefore submitted to estimation from the experimental results.

In this program, a sensitivity analysis of the kinetic parameters of the reaction mechanism allows the detection of those elementary steps which are negligible ( $\sigma_{ij} = 0$  for  $k_i = 0$ ), not determining ( $\sigma_i \approx 0$  for  $\Delta k_i / k_i = 10$ ) and determining ( $\sigma_{ij} \neq 0$  for  $\Delta k_i / k_i = 10$ ).

Using this technique, we have been able to reduce the initial number of elementary steps from 72 to 35.

### REACTION MECHANISM AND MODEL

The thermal cracking of 3-methylpentane yields methane, ethane, 2-butane, 2-methyl-1-butene, ethylene and propylene as major products with relatively smaller amounts of *trans*-2-pentene, 1-butene and hydrogen [4].

The simplified mechanism included three elementary initiation steps by scission of C–C bonds and one by scission of a C–H bond; the 3-methylpentane molecule decomposes via four closed sequences corresponding to the unimolecular decomposition of the isomeric forms of the methylpentyl radicals denoted by  $m_1$ ,  $m_2$ ,  $m_3$  and  $m_4$ . In the symbolism proposed by Goldfinger et al. [7] the radicals are denoted by  $\mu'$  and are derived from the alkane molecule  $\mu\text{H}$  (in this case 3-methylpentane) by hydrogen transfer (metathesis) by the chain carriers such as  $\text{H}^\cdot$ ,  $\text{CH}_3^\cdot$  and  $\text{C}_2\text{H}_5^\cdot$ , producing methylpentyl radicals and respectively  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . Taking into account the results of the sensitivity analysis, we also include the hydrogen transfer by  $2\text{-C}_4\text{H}_9^\cdot$  radicals leading to the formation of  $n\text{-C}_4\text{H}_{10}$  which has been found in the reaction products.

Therefore the reaction scheme includes, as mentioned above, the unimolecular decomposition step of the four isomeric  $\mu'$  radicals, but also those of  $\text{C}_2\text{H}_5^\cdot$  and  $\text{C}_4\text{H}_9^\cdot$ , and the subsequent steps. The other unimolecular decompositions are considered negligible.

### RESULTS AND DISCUSSION

Simulations using the mechanistic model comprising 35 elementary steps have been performed on a SUN computer (UNIX system). Table 1 and Fig. 2 show the comparisons of experimental and simulated product formation versus time. The yields of the major products versus time show fairly good

TABLE 1

Comparison of experimental (exp) and simulated (s) product concentration ( $\text{mol cm}^{-3} \times 10^9$ ); initial mechanism, 35 steps ( $C_6H_{14,0} = 0.23 \times 10^{-5} \text{ mol cm}^{-3}$ )

$t$ (s)	$CH_4$ (exp)	$CH_4$ (s)	$C_2H_6$ (exp)	$C_2H_6$ (s)	$C_2H_4$ (exp)	$C_2H_4$ (s)	$C_2H_2$ (exp)	$C_2H_2$ (s)	$C_2H_4$ (exp)	$C_2H_4$ (s)	$C_2H_6$ (exp)	$C_2H_6$ (s)	$C_3H_8$ (exp)	$C_3H_8$ (s)
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
60	1.52	1.45	1.15	0.77	0.57	0.32	0.46	0.29	0.46	0.32	0.46	0.29	0.46	0.29
120	2.33	2.31	1.76	1.54	0.83	0.65	0.70	0.58	0.83	0.65	0.70	0.58	0.83	0.58
180	2.91	4.37	2.17	2.32	1.03	0.98	0.85	0.87	1.03	0.98	0.85	0.87	1.03	0.87
240	3.8	5.28	2.80	3.09	1.30	1.31	1.11	1.16	1.30	1.31	1.11	1.16	1.30	1.16
300	4.05	7.27	2.98	3.86	1.41	1.63	1.18	1.44	1.41	1.63	1.18	1.44	1.41	1.44
$t$ (s)	$1-C_4H_8$ (exp)	$1-C_4H_8$ (s)	$2-C_4H_8$ (exp)	$2-C_4H_8$ (s)	$C_5H_{10}$ (exp)	$C_5H_{10}$ (s)	$C_5H_{10}$ (exp)	$C_5H_{10}$ (s)	$C_5H_{10}$ (exp)	$C_5H_{10}$ (s)	$C_5H_{10}$ (exp)	$C_5H_{10}$ (s)	$C_5H_{10}$ (exp)	$C_5H_{10}$ (s)
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
60	0.16	0.31	1.14	0.48	0.16	0.45	0.16	0.45	0.16	0.45	0.16	0.45	0.16	0.45
120	0.23	0.63	1.59	0.96	0.25	0.90	0.25	0.90	0.25	0.90	0.25	0.90	0.25	0.90
180	0.29	0.94	1.90	1.44	0.32	1.35	0.32	1.35	0.32	1.35	0.32	1.35	0.32	1.35
240	0.37	1.25	2.43	1.92	0.39	1.8	0.39	1.8	0.39	1.8	0.39	1.8	0.39	1.8
300	0.43	1.57	2.60	2.40	0.43	2.24	0.43	2.24	0.43	2.24	0.43	2.24	0.43	2.24



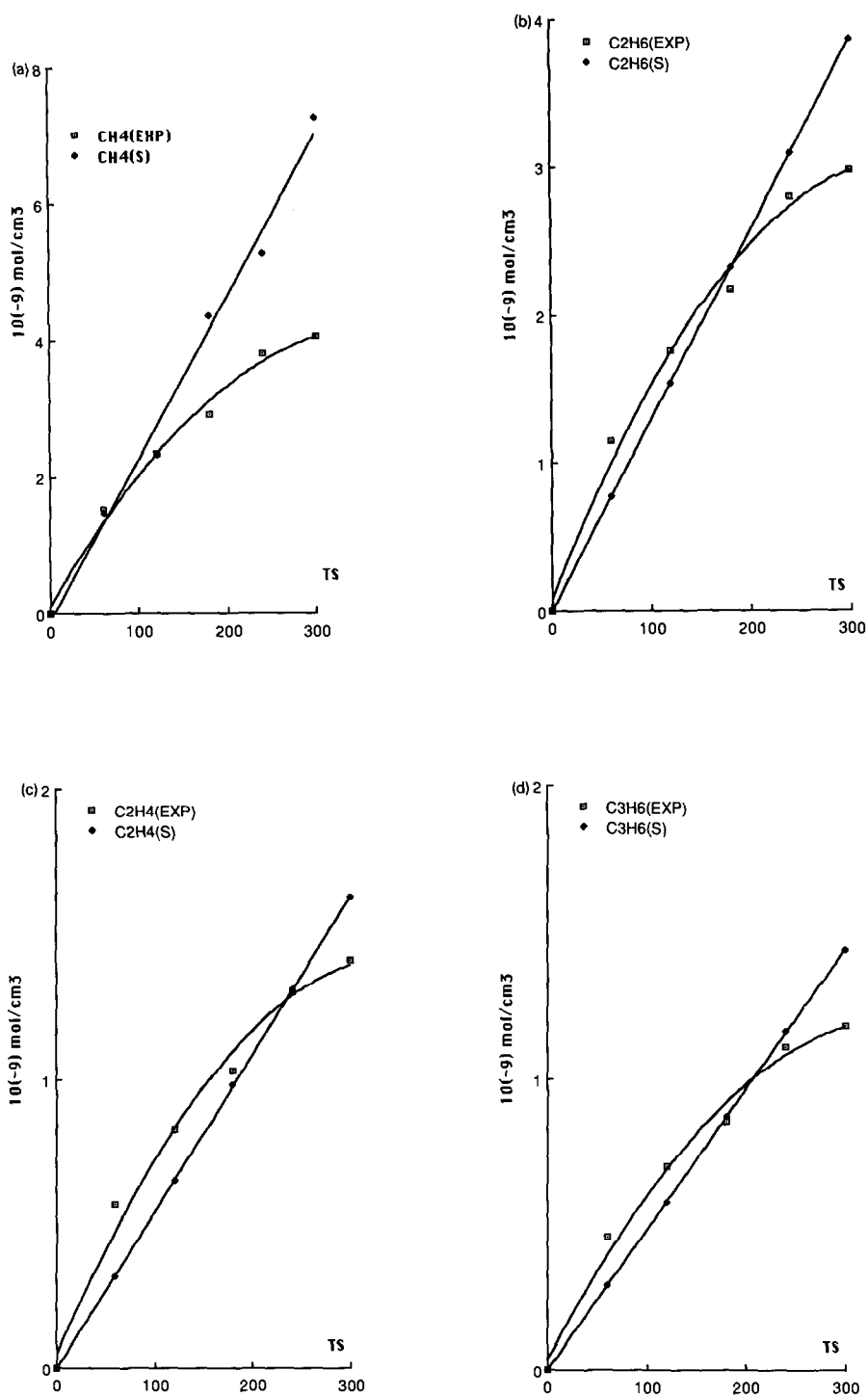


Fig. 2. a to g, Experimental and simulated main product concentrations in the pyrolysis of 3-methylpentane at 420 °C (initial mechanism).

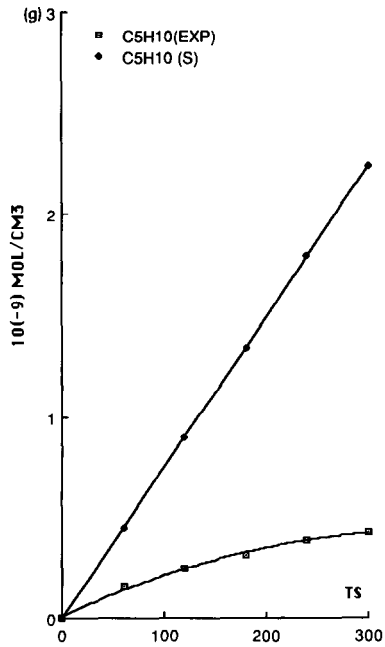
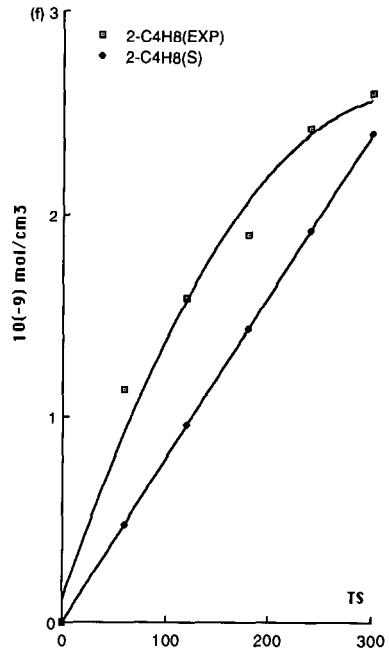
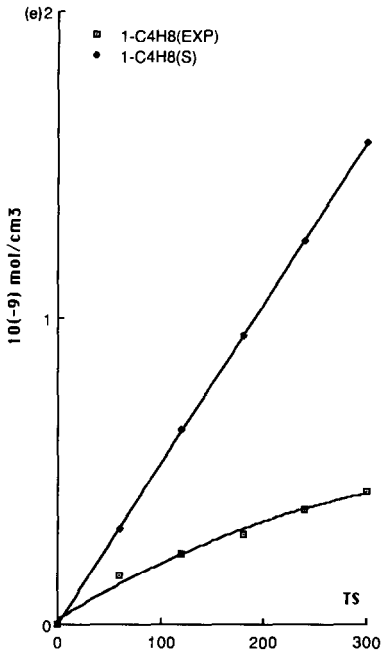


Fig. 2 (continued).

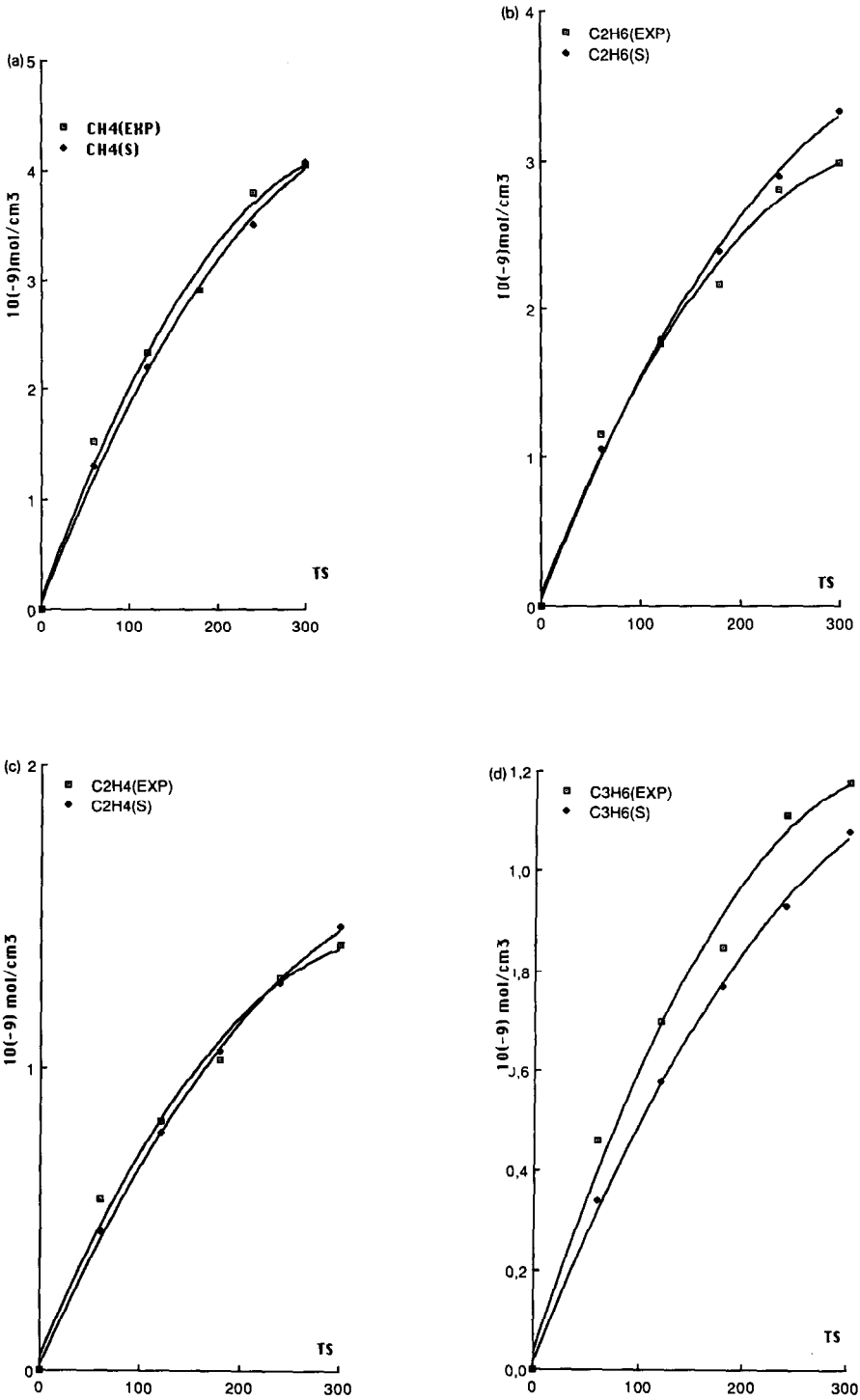


Fig. 3. a to i, Experimental and simulated concentrations of the main reaction products in the 3-methylpentane pyrolysis at 420°C (mechanism of Table 2).

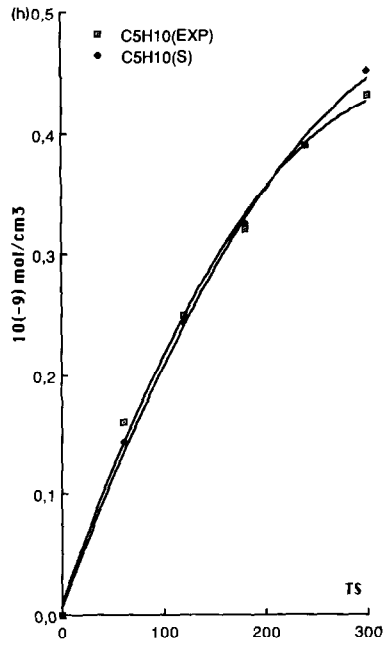
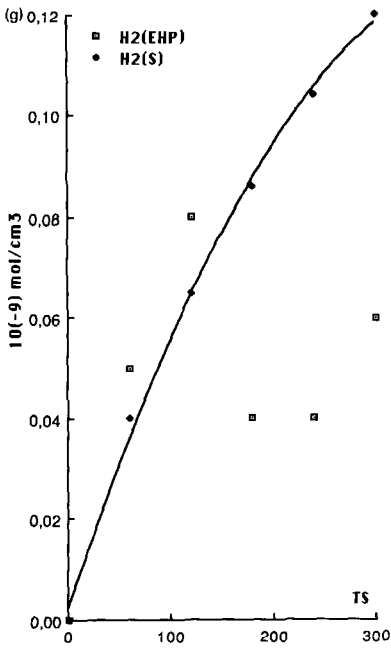
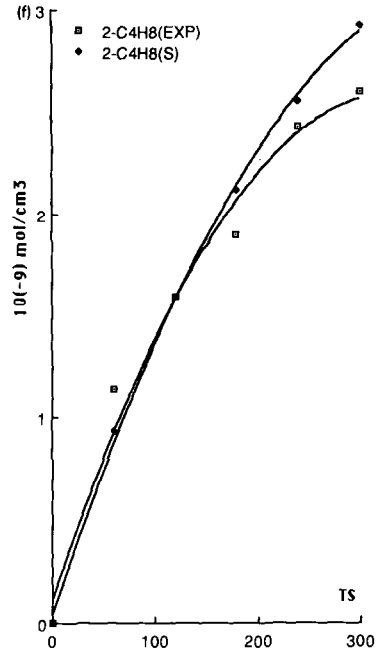
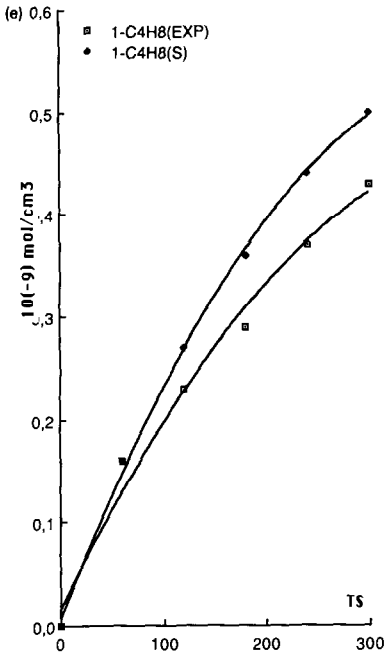


Fig. 3 (continued).

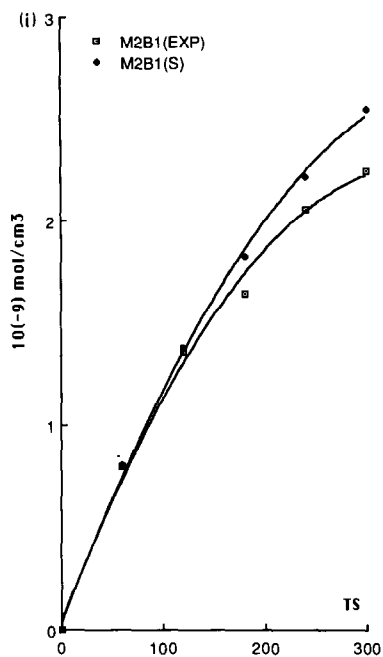
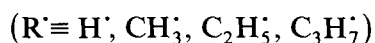
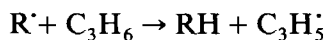


Fig. 3 (continued).

agreement between experimental and computed curves during the first stages of the reaction but this model does not explain the self-inhibition of the pyrolysis of 3-methylpentane.

The important reactions accounting for inhibition (or self-inhibition) by olefins are the addition of  $H^\cdot$  (and perhaps  $CH_3^\cdot$ ) on the double bond of these molecules, and the hydrogen abstraction from these olefins by the same species (especially  $H^\cdot$  and  $CH_3^\cdot$ ), to give stable, rather unreactive products, because they are stabilised by resonance



The rate parameters for the elementary steps are listed in Table 2 and are largely derived from the values published by Allara and Shaw [8]. Some of these rate parameters have also been modified within a limited range in order to improve the fitting of the computed curves with the experimental results.

Table 3 shows the comparison of experimental and simulated results for the pyrolysis of 3-methylpentane. A fitting of the rate parameters has been performed to test our model.

Figure 3 describes the formation of the major reaction products (see Table 3) in which we compare the experimental and the fitted curves.

TABLE 2  
Mechanistic model for the pyrolysis of 3-methylpentane<sup>a</sup>

Step <sup>b</sup>	A	E	Reference	Initial value (693 K)	Adjusted value (693 K)
<b>Initiation</b>					
1	$C_6H_{14} \rightarrow CH_3^{\cdot}$ $+ r_1$	85400	c	$0.7359457 \times 10^{-10}$	$0.7359457 \times 10^{-10}$
2	$C_6H_{14} \rightarrow CH_3^{\cdot}$ $+ r_2$	82900	c	$0.7176739 \times 10^{-9}$	$0.7176739 \times 10^{-9}$
3	$C_6H_{14} \rightarrow C_2H_5^{\cdot}$ $+ 2-C_4H_9$	79200	c	$0.6639452 \times 10^{-9}$	$0.2439452 \times 10^{-7}$
4	$C_6H_{14} \rightarrow H^{\cdot}$ $+ m_1$	78000	c	$0.6297588 \times 10^{-11}$	$0.6297588 \times 10^{-11}$
<b>Transfer</b>					
5	$H^{\cdot} + C_6H_{14} \rightarrow H_2$ $+ m_1$	9700	c	$0.1091020 \times 10^{12}$	$0.1091020 \times 10^{12}$
6	$H^{\cdot} + C_6H_{14} \rightarrow H_2$ $+ m_2$	7100	c	$0.2888812 \times 10^{13}$	$0.2888812 \times 10^{13}$
7	$H^{\cdot} + C_6H_{14} \rightarrow H_2$ $+ m_3$	7100	c	$0.2888812 \times 10^{13}$	$0.2888812 \times 10^{13}$
8	$H^{\cdot} + C_6H_{14} \rightarrow H_2$ $+ m_4$	7100	c	$0.2888812 \times 10^{13}$	$0.2888812 \times 10^{13}$
9	$CH_3^{\cdot} + C_6H_{14} \rightarrow CH_4$ $+ m_1$	11400	c	$0.1010832 \times 10^9$	$0.1010832 \times 10^9$
10	$CH_3^{\cdot} + C_6H_{14} \rightarrow CH_4$ $+ m_2$	9600	c	$0.5274678 \times 10^9$	$0.5274678 \times 10^9$
11	$CH_3^{\cdot} + C_6H_{14} \rightarrow CH_4$ $+ m_3$	9600	c	$0.3688520 \times 10^9$	$0.2688520 \times 10^9$
12	$CH_3^{\cdot} + C_6H_{14} \rightarrow CH_4$ $+ m_4$	11400	c	$0.1010832 \times 10^9$	$0.1010832 \times 10^9$
13	$C_2H_5^{\cdot} + C_6H_{14} \rightarrow C_2H_6$ $+ m_1$	12300	c	$0.4174947 \times 10^8$	$0.4174947 \times 10^8$
14	$C_2H_5^{\cdot} + C_6H_{14} \rightarrow C_2H_6$ $+ m_2$	10400	c	$0.5250064 \times 10^8$	$0.5250064 \times 10^8$
15	$C_2H_5^{\cdot} + C_6H_{14} \rightarrow C_2H_6$ $+ m_3$	10400	c	$0.5250064 \times 10^8$	$0.5250064 \times 10^8$
16	$C_2H_5^{\cdot} + C_6H_{14} \rightarrow C_2H_6$ $+ m_4$	12300	c	$0.4174947 \times 10^8$	$0.0174947 \times 10^8$
17	$2-C_4H_9^{\cdot} + C_6H_{14} \rightarrow C_4H_{10}$ $+ m_1$	12900	c	$0.8545601 \times 10^7$	$0.8545601 \times 10^7$
18	$2-C_4H_9^{\cdot} + C_6H_{14} \rightarrow C_4H_{10}$ $+ m_2$	10400	c	$0.5250064 \times 10^8$	$0.5250064 \times 10^8$
19	$2-C_4H_9^{\cdot} + C_6H_{14} \rightarrow C_4H_{10}$ $+ m_3$	10400	c	$0.5250064 \times 10^8$	$0.4250064 \times 10^8$
20	$2-C_4H_9^{\cdot} + C_6H_{14} \rightarrow C_4H_{10}$ $+ m_4$	12900	c	$0.8546501 \times 10^7$	$0.8546501 \times 10^7$
25	$C_3H_6^{\cdot} + s-C_3H_7 \rightarrow C_3H_8$ $+ C_3H_5$	10800	[8]	$0.3889000 \times 10^8$	$0.5433295 \times 10^8$
26	$C_3H_6^{\cdot} + C_2H_5^{\cdot} \rightarrow C_2H_6$ $+ C_3H_5$	8300	c	$0.1199802 \times 10^{10}$	$0.1199802 \times 10^{10}$
<b>Addition</b>					
21	$H^{\cdot} + C_2H_4 \rightarrow C_2H_5^{\cdot}$	2600	[8]	$0.6012241 \times 10^{13}$	$0.1132123 \times 10^{13}$
22	$H^{\cdot} + C_3H_6 \rightarrow s-C_3H_7^{\cdot}$	1200	[8]	$0.3305100 \times 10^{13}$	$0.3364704 \times 10^{13}$

23	H <sup>•</sup>	+C <sub>3</sub> H <sub>6</sub>	→ H <sub>2</sub>	1 × 10 <sup>14</sup>	3500	[8]	0.7874251 × 10 <sup>13</sup>	0.7874251 × 10 <sup>13</sup>
24	CH <sub>3</sub>	+C <sub>3</sub> H <sub>6</sub>	→ CH <sub>4</sub>	1.58 × 10 <sup>11</sup>	8800	[8]	0.2651012 × 10 <sup>9</sup>	0.2651012 × 10 <sup>9</sup>
Decomposition								
27	m <sub>1</sub>	+2-C <sub>4</sub> H <sub>9</sub>	→ 2-C <sub>4</sub> H <sub>9</sub>	3.98 × 10 <sup>12</sup>	26200	[8]	0.2173806 × 10 <sup>5</sup>	0.2173806 × 10 <sup>5</sup>
28	m <sub>2</sub>	+C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>5</sub>	5.00 × 10 <sup>12</sup>	29100	c	0.3324591 × 10 <sup>4</sup>	0.3324591 × 10 <sup>4</sup>
29	m <sub>3</sub>	+CH <sub>3</sub>	→ CH <sub>3</sub>	7.94 × 10 <sup>13</sup>	33000	c	0.3109212 × 10 <sup>4</sup>	0.3109212 × 10 <sup>4</sup>
30	m <sub>4</sub>	+1-C <sub>4</sub> H <sub>8</sub>	→ C <sub>2</sub> H <sub>5</sub>	1.25 × 10 <sup>13</sup>	29500	c	0.6216281 × 10 <sup>4</sup>	0.6216281 × 10 <sup>4</sup>
31	m <sub>2</sub>	+2-C <sub>3</sub> H <sub>10</sub>	→ CH <sub>3</sub>	7.94 × 10 <sup>13</sup>	33000	c	0.3109212 × 10 <sup>4</sup>	0.3109212 × 10 <sup>4</sup>
32	2-C <sub>4</sub> H <sub>9</sub>	+C <sub>3</sub> H <sub>6</sub>	→ CH <sub>3</sub>	1.33 × 10 <sup>14</sup>	33200	[8]	0.4504097 × 10 <sup>4</sup>	0.4504097 × 10 <sup>4</sup>
33	C <sub>2</sub> H <sub>5</sub>	+C <sub>3</sub> H <sub>4</sub>	→ H <sup>•</sup>	3.98 × 10 <sup>13</sup>	40500	[8]	0.7771785 × 10 <sup>1</sup>	0.7771785 × 10 <sup>1</sup>
34	2-C <sub>4</sub> H <sub>9</sub>	+1-C <sub>4</sub> H <sub>8</sub>	→ H <sup>•</sup>	1.99 × 10 <sup>13</sup>	40400	[8]	0.3613715 × 10 <sup>1</sup>	0.3613715 × 10 <sup>1</sup>
35	2-C <sub>4</sub> H <sub>9</sub>	+2-C <sub>4</sub> H <sub>8</sub>	→ H <sup>•</sup>	5.01 × 10 <sup>12</sup>	37900	[8]	0.5589340 × 10 <sup>1</sup>	0.5589340 × 10 <sup>1</sup>
36	C <sub>2</sub> H <sub>5</sub>	+H <sup>•</sup>	→ C <sub>2</sub> H <sub>4</sub>	3.16 × 10 <sup>13</sup>	40800	[8]	0.4291809 × 10 <sup>1</sup>	0.4291809 × 10 <sup>1</sup>
37	s-C <sub>3</sub> H <sub>7</sub>	+C <sub>3</sub> H <sub>6</sub>	→ H <sup>•</sup>	7.9 × 10 <sup>13</sup>	40400	[8]	0.1060283 × 10 <sup>2</sup>	0.1060283 × 10 <sup>2</sup>
Termination								
38	H <sup>•</sup>	+CH <sub>3</sub>	→ CH <sub>4</sub>	1.99 × 10 <sup>14</sup>	0	[9]	0.1990000 × 10 <sup>15</sup>	0.1990000 × 10 <sup>15</sup>
39	CH <sub>3</sub>	+CH <sub>3</sub>	→ C <sub>2</sub> H <sub>6</sub>	2.51 × 10 <sup>13</sup>	0	[10]	0.2510000 × 10 <sup>14</sup>	0.2510000 × 10 <sup>14</sup>
40	CH <sub>3</sub>	+C <sub>2</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>8</sub>	2.00 × 10 <sup>13</sup>	0	[8]	0.2000000 × 10 <sup>14</sup>	0.2000000 × 10 <sup>14</sup>
41	C <sub>2</sub> H <sub>5</sub>	+C <sub>2</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>10</sub>	3.98 × 10 <sup>12</sup>	0	[11]	0.3980000 × 10 <sup>13</sup>	0.3980000 × 10 <sup>13</sup>
42	C <sub>2</sub> H <sub>5</sub>	+C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub>	5.01 × 10 <sup>12</sup>	0	[12]	0.5010000 × 10 <sup>12</sup>	0.5010000 × 10 <sup>12</sup>
43	CH <sub>3</sub>	+C <sub>3</sub> H <sub>5</sub>	→ 1-C <sub>4</sub> H <sub>8</sub>	1.99 × 10 <sup>13</sup>	0	[13]	0.1990000 × 10 <sup>14</sup>	0.1990000 × 10 <sup>14</sup>
44	C <sub>3</sub> H <sub>7</sub>	+CH <sub>3</sub>	→ 1-C <sub>4</sub> H <sub>10</sub>	1.6 × 10 <sup>13</sup>	0	[8]	0.1600000 × 10 <sup>14</sup>	0.1600000 × 10 <sup>14</sup>

<sup>a</sup> Rate constants are expressed in the units cm<sup>3</sup>, mol and s, and are calculated for 420 °C (1093 K) and 100 Torr. The temperature dependence is given by  $k = Ae^{-E/RT}$ .

<sup>b</sup> m<sub>1</sub> = CH<sub>3</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>; M<sub>2</sub>B<sub>1</sub> = CH<sub>3</sub>-CH<sub>2</sub>-C(CH<sub>3</sub>)-CH<sub>2</sub>;

m<sub>2</sub> = CH<sub>3</sub>-CH'-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>; 2-C<sub>4</sub>H<sub>8</sub> = CH<sub>3</sub>-CH = CH-CH<sub>3</sub>;

m<sub>3</sub> = CH<sub>3</sub>-CH<sub>2</sub>-C'(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>; 2-C<sub>4</sub>H<sub>10</sub> = CH<sub>3</sub>-CH = CH-CH<sub>2</sub>-CH<sub>3</sub>;

m<sub>4</sub> = CH<sub>3</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>; 1-C<sub>4</sub>H<sub>8</sub> = CH<sub>2</sub> = CH-CH<sub>2</sub>-CH<sub>3</sub>;

r<sub>1</sub> = CH<sub>3</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>;

r<sub>2</sub> = CH<sub>3</sub>-CH<sub>2</sub>-CH'-CH<sub>2</sub>-CH<sub>3</sub>;

<sup>c</sup> Estimated by the authors. i-C<sub>4</sub>H<sub>10</sub> = CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>3</sub>.





There is a rather good agreement between our experimental results and the computed curves derived from our basic model to which we have added the elementary steps accounting for the auto-inhibition (44 elementary steps) at 420°C and 133 mbar. This suggests that the model gives a reasonably good account of the reaction, including the self-inhibition, within our range of residence times (1–5 min).

In the case of hydrogen (Fig. 3), taking into account the limited amounts formed and the lower sensitivity of the detector (thermistors), the resulting scattering of the experimental data is not really surprising.

## CONCLUSION

The thermal decomposition of 3-methylpentane which takes place through a rather complicated chain free-radical mechanism has been investigated. Taking into account the experimental results, we have put forward a reaction mechanism involving 72 elementary steps. A sensitivity analysis has allowed us to reduce this number; considering the self-inhibition of the reaction, 44 elementary steps have been included in our model.

We have obtained a satisfactory agreement between computed and experimental results, using the MORSE package.

The present work shows that these modelling techniques can substantially contribute to a better understanding of complicated reaction mechanisms.

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