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Thermal decomposition of pure methane at 1263 K. Experiments and mechanistic modelling

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Abstract

Pyrolysis of methane at 1263 K and at normal pressure was carried out in an alumina tube (length, 610 mm; inside diameter, 12 mm; outside diameter, 18 mm), which was heated by an electric furnace. The input concentration of CH_4 was 10.308×10^{-6} mol cm^{-3}. The reaction times ranged between 0.457 and 6 s. The products were analyzed by two chromatographs. Carbon monoxide and carbon dioxide were analyzed by an IR spectrometer. A reaction model, based on 119 elementary reactions, was developed to predict the experimental results and to verify the data basis on elementary reactions under the conditions of temperature studied. The model gives a quantitative description of the complex chemistry of the process and the information of products from C_2 to C_6H_6.

INTRODUCTION

In the near future, natural gas will play an increasing role as a source of raw materials for the petrochemical industry and liquid fuels.

As recent estimates show, world reserves of natural gas are larger than those of crude oil [1]. The greatest problem to solve is the cost of the transport of the natural gas (the natural gas is liquefied at −160°C).

To develop remote gasfields and to develop the natural gas industry on a large scale, conversion at the natural gas field may be most realistic.

For more than a century, the steam reforming reaction of methane has been well established, leading to a synthesis gas that is a mixture of hydrogen and carbon monoxide ($3H_2 + CO$). This synthesis gas can then

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be used to make either methanol or liquid fuels. These processes are well known and their disadvantages are cost and large energy requirements: because of the great stability of the methane molecule the steam reforming process is highly endothermic.

Therefore, since the 1978 energy crisis considerable effort has been devoted to opening up other channels for the conversion of natural gas into alcohols and higher hydrocarbons, without the step of making the synthesis gas [2, 3].

In this study, we look at a direct route for the conversion of methane into higher hydrocarbons.

EXPERIMENTAL AND RESULTS

Experimental

Flowsheet of the micropilot plant

A simplified flowsheet of the micropilot that was used is shown in Fig. 1 (see also ref. 2). The flow rate was about 15 l h^{-1}. The reactor was

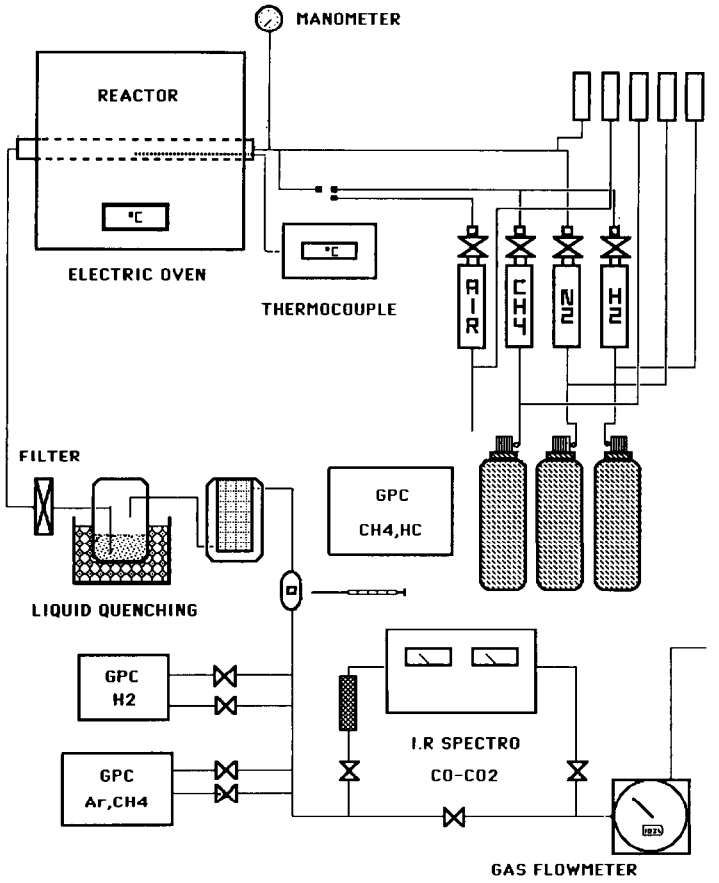


Fig. 1. Flowsheet of the micropilot plant.

TABLE 1

Experimental product concentrations (10^{-6} mol l^{-1})

	Time (s)														
Molecule [a]	0.457	0.508	0.572	0.654	0.763	0.918	1.14	1.526	1.907	2.29	2.74	3.2	4.57	5.5	6.0
H_2	8.15	9.38	11.15	13.62	17.75	24.46	37.05	65.23	101.16	138.81	210.4	387.6	590.	853.	916.7
C_2H_4	1.56	1.71	2.01	2.53	3.41	3.98	6.48	10.47	18.19	19.24	23.66	30.25	50.1	64.24	73.40
C_2H_2	–	–	–	0.07	0.13	0.18	0.35	0.66	1.41	2.52	3.66	6.04	13.50	16.93	16.93
C_2H_6	3.56	3.32	3.50	3.87	4.11	4.29	5.08	5.23	6.74	6.44	6.99	7.49	8.08	8.58	7.73
C_3H_6	–	0.09	0.09	0.13	0.20	0.29	0.57	1.12	2.26	2.44	3.10	4.09	6.31	6.88	7.02
a-C_3H_4	–	–	–	–	0.02	0.03	0.1	0.23	0.55	0.75	1.065	1.23	1.70	1.39	1.22
p-C_2H_4	–	–	–	–	0.05	0.09	0.24	0.57	1.22	1.98	2.72	3.65	4.80	4.06	3.54
C_4H_6	–	–	–	–	–	–	0.04	0.14	0.39	0.39	0.81	1.06	1.47	1.22	1.14
C_5H_6	–	–	–	–	–	–	–	0.12	0.14	0.21	0.33	0.57	1.00	1.02	1.0
C_6H_6	–	–	–	–	–	–	–	0.14	0.15	0.32	0.76	1.72	6.78	9.75	11.91
CH_4 [b]	10.308	10.306	10.305	10.296	10.295	10.293	10.272	10.237	10.189	10.148	10.061	9.976	9.635	9.345	9.1667

[a] For abbreviated structures see Appendix, Table A2.

[b] 10^{-3} mol l^{-1} (see text).

an alumina tube (length = 610 mm, inside diameter = 12 mm, outside diameter = 18 mm) heated by an electric furnace. The temperature was controlled by a thermocouple (type S) inside the main tube.

During the pyrolysis step, an analysis was performed by gas chromatography. Hydrogen was determined online by GC-TCD (DELSI-IGC 1). Hydrocarbons were analyzed offline by a GC (DELSI-DI200) equipped with a capillary column (HP special PONA; 50 meters). To measure all the hydrocarbons and especially the light products (CH_4, C_2H_2, C_2H_4, ...), the temperature programming was started at −60°C. Liquid hydrocarbons were analyzed with the same column by the intern standard method (ethylbenzene). The heavier hydrocarbons were collected in quartz wool and weighted after each run.

Another GC-TCD (HP 5890) was used for the measure of the CH_4 conversion by the analysis of argon injected in small quantities in the inlet flow.

By doing a series of analyses before and during a run, we obtain the conversion of the methane as

$$X = \frac{(CH_4/Ar)^\circ - (CH_4/Ar)}{(CH_4/Ar)^\circ}$$

To measure the coke formed during the reaction, the reactor was decoked by a mixture of air and nitrogen at 1000°C. The carbon monoxide and carbon dioxide produced during decoking were measured on-line by an IR spectrometer (COSMA).

The C and H material balance was determined by integrating total flow rates and analyses.

Results

The initial concentration of methane was 10.308×10^{-6} mol cm^{-3}. The various results obtained at 1263 K and 760 torr are summarized in Table 1.

REACTION MECHANISM AND MODEL

Introduction — the mechanism of Roscoe and Thomson [4]

In the literature the mechanisms of Roscoe and Thompson [4] and Back and co-workers [5] take into account the light products and are valid only for small reaction extents.

The mechanism of the thermal decomposition of methane that best explains the formation of hydrogen, ethane, ethene, propene and acetylene is probable that proposed by Chen and Back [5], who have proposed several kinds of elementary reactions (ERs): primary formation of ethane and hydrogen; secondary reactions of ethane; secondary reactions of ethylene; secondary reactions of acetylene.

TABLE 2

Mechanistic model for the pyrolysis of methane by Roscoe and Thompson

ER No.	ER [a]		a_d [b]	k_d [c]	e_d [d]
⟨1⟩	CH_4	$\rightarrow CH_3\cdot + H\cdot$	7.7×10^{15}		1.07×10^5
⟨2⟩	C_2H_6	$\rightarrow CH_3\cdot + CH_3\cdot$	6.49×10^{16}		8.90×10^4
⟨3⟩	C_2H_6	$\rightarrow C_2H_5\cdot + H\cdot$	8.88×10^{15}		9.776×10^4
⟨4⟩	C_3H_6	$\rightarrow C_3H_5\cdot + H\cdot$	9.16×10^{14}		8.782×10^4
⟨5⟩	C_3H_6	$\rightarrow CH_3\cdot + C_2H_3\cdot$	1.34×10^{16}		8.842×10^4
⟨6⟩	C_3H_6	$\rightarrow$ '$C_3H_5\cdot$' $+ H\cdot$	2.28×10^{16}		96.6×10^3
⟨7⟩	$C_2H_4 + C_2H_4$	$\rightarrow C_2H_5\cdot + C_2H_3\cdot$	1.86×10^{14}		2.782×10^4
⟨8⟩	$H\cdot + CH_4$	$\rightarrow H_2 + CH_3\cdot$	1.26×10^{11}		1.258×10^4
⟨9⟩	$C_2H_5\cdot + CH_4$	$\rightarrow C_2H_6 + CH_3\cdot$	1.0×10^{11}		1.099×10^4
⟨10⟩	$C_2H_3\cdot + CH_4$	$\rightarrow C_2H_4 + CH_3\cdot$	3.5×10^{12}		1.597×10^4
⟨11⟩	$C_3H_5\cdot + CH_4$	$\rightarrow C_3H_6 + CH_3\cdot$	1.29×10^{10}		1.59×10^4
⟨12⟩	'$C_3H_5\cdot$' $+ CH_4$	$\rightarrow C_3H_6 + CH_3\cdot$	6.31×10^{12}		15.97×10^3
⟨13⟩	$CH_3\cdot + H_2$	$\rightarrow CH_4 + H\cdot$	3.16×10^{12}		1.02×10^4
⟨14⟩	$C_2H_5\cdot + H_2$	$\rightarrow C_2H_6 + H\cdot$	3.98×10^{12}		1.4×10^4
⟨15⟩	$C_2H_3\cdot + H_2$	$\rightarrow C_2H_4 + H\cdot$	7.94×10^{12}		7.39×10^3
⟨16⟩	$C_3H_5\cdot + H_2$	$\rightarrow C_3H_6 + H\cdot$	3.16×10^{13}		1.969×10^4
⟨17⟩	'$C_3H_5\cdot$' $+ H_2$	$\rightarrow C_3H_6 + H\cdot$	7.9×10^{12}		7.39×10^3
⟨18⟩	$H\cdot + C_2H_6$	$\rightarrow C_2H_5\cdot + H_2$	1.26×10^{14}		9.696×10^3
⟨19⟩	$CH_3\cdot + C_2H_6$	$\rightarrow CH_4 + C_2H_5\cdot$	3.16×10^{13}		2.086×10^4
⟨20⟩	$C_3H_5\cdot + C_2H_6$	$\rightarrow C_3H_6 + C_2H_5\cdot$	7.94×10^{11}		2.047×10^4
⟨21⟩	'$C_3H_5\cdot$' $+ C_2H_6$	$\rightarrow C_3H_6 + C_2H_3\cdot$	8.83×10^{10}		15.97×10^3
⟨22⟩	$C_2H_3\cdot + C_2H_6$	$\rightarrow C_2H_4 + C_2H_5\cdot$	6.48×10^{13}		1.597×10^4
⟨23⟩	$H\cdot + C_2H_4$	$\rightarrow H_2 + C_2H_3\cdot$	3.16×10^{11}		4.49×10^3
⟨24⟩	$CH_3\cdot + C_2H_4$	$\rightarrow CH_4 + C_2H_3\cdot$	6.06×10^{10}		7.988×10^3
⟨25⟩	$C_2H_5\cdot + C_2H_4$	$\rightarrow C_2H_6 + C_2H_3\cdot$	3.16×10^{11}		1.087×10^4
⟨26⟩	$H\cdot + C_3H_6$	$\rightarrow H_2 + C_3H_5\cdot$	1.0×10^{14}		3.497×10^3
⟨27⟩	$H\cdot + C_3H_6$	$\rightarrow H_2 +$ '$C_3H_5\cdot$'	1.76×10^{11}		4.49×10^3
⟨28⟩	$CH_3\cdot + C_3H_6$	$\rightarrow CH_4 + C_3H_5\cdot$	1.38×10^{11}		8.80×10^3
⟨29⟩	$CH_3\cdot + C_3H_6$	$\rightarrow CH_4 +$ '$C_3H_5\cdot$'	1.6×10^{11}		10.97×10^3
⟨30⟩	$C_2H_5\cdot + C_3H_6$	$\rightarrow C_2H_6 + C_3H_5\cdot$	2.0×10^{10}		4.49×10^3
⟨31⟩	$C_2H_5\cdot + C_3H_6$	$\rightarrow C_2H_6 +$ '$C_3H_5\cdot$'	2.04×10^{11}		10.97×10^3
⟨32⟩	$C_2H_5\cdot$	$\rightarrow C_2H_4 + H\cdot$	1.7×10^{12}		4.093×10^4
⟨33⟩	$C_2H_3\cdot$	$\rightarrow C_2H_2 + H\cdot$	0.63×10^9		3.14×10^4
⟨34⟩	'n-$C_3H_7\cdot$'	$\rightarrow C_3H_6 + H\cdot$	1.58×10^{13}		3.85×10^4
⟨35⟩	'n-$C_3H_7\cdot$'	$\rightarrow C_2H_4 + CH_3\cdot$	0.76×10^{13}		3.259×10^4
⟨36⟩	'i-$C_3H_7\cdot$'	$\rightarrow C_3H_6 + H\cdot$	7.94×10^{13}		4.03×10^4
⟨37⟩	'$C_3H_5\cdot$'	$\rightarrow$ 'p-C_3H_4' $+ H\cdot$	2.45×10^9		31.4×10^3
⟨38⟩	'$C_3H_5\cdot$'	$\rightarrow C_2H_2 + CH_3\cdot$	0.79×10^{12}		3.76×10^4
⟨39⟩	$C_3H_5\cdot$	$\rightarrow a$-$C_3H_4 + H\cdot$	2.5×10^{13}		5.90×10^4
⟨40⟩	'i-$C_4H_9\cdot$'	$\rightarrow$ 'i-C_4H_8' $+ H\cdot$	2.0×10^{13}		4.03×10^4
⟨41⟩	'i-$C_4H_9\cdot$'	$\rightarrow C_3H_6 + CH_3\cdot$	2.0×10^{14}		3.32×10^4
⟨42⟩	'p-$C_4H_9\cdot$'	$\rightarrow$ 'i-C_4H_8' $+ H\cdot$	1.26×10^{13}		3.85×10^4
⟨43⟩	'p-$C_4H_9\cdot$'	$\rightarrow C_2H_4 + C_2H_5\cdot$	2.51×10^{13}		2.88×10^4
⟨44⟩	'p-$C_4H_9\cdot$'	$\rightarrow C_3H_6 + CH_3\cdot$	1.25×10^{12}		2.16×10^4
⟨45⟩	$C_2H_4 + H\cdot$	$\rightarrow C_2H_5\cdot$	1.14×10^{14}		2.6×10^3
⟨46⟩	$C_2H_2 + H\cdot$	$\rightarrow C_2H_3\cdot$	1.85×10^{13}		1.297×10^3
⟨47⟩	$C_2H_4 + CH_3\cdot$	$\rightarrow$ 'n-$C_3H_7\cdot$'	4.18×10^{11}		7.71×10^3
⟨48⟩	$C_3H_6 + H\cdot$	$\rightarrow$ 'n-$C_3H_7\cdot$'	7.94×10^{12}		2.9×10^3
⟨49⟩	$C_2H_2 + CH_3\cdot$	$\rightarrow$ '$C_3H_5\cdot$'	1.9×10^9		7.67×10^2
⟨50⟩	$C_3H_6 + H\cdot$	$\rightarrow$ 'i-$C_3H_7\cdot$'	7.94×10^{12}		1.2×10^3
⟨51⟩	$C_2H_4 + C_2H_5\cdot$	$\rightarrow$ 'p-$C_4H_9\cdot$'	6.31×10^{10}		7.59×10^3

TABLE 2 (continued)

ER No.	ER [a]		a_d [b]	k_d [c]	e_d [d]
⟨52⟩	'p-C_3H_4' + H·	→ 'C_3H_5·'	3.47×10^{13}		1.987×10^3
⟨53⟩	'a-C_3H_4' + H·	→ C_3H_5·	8.33×10^{13}		1.987×10^3
⟨54⟩	$C_3H_6 + CH_3$·	→ 'i-C_4H_9·'	3.16×10^{11}		7.39×10^3
⟨55⟩	'i-C_4H_8' + H·	→ 'i-C_4H_9·'	7.94×10^{12}		1.2×10^3
⟨56⟩	'n-C_3H_7·'	→ 'i-C_3H_7·'	2.51×10^{12}		3.398×10^4
⟨57⟩	'i-C_3H_7·'	→ 'n-C_3H_7·'	1×10^{13}		3.795×10^4
⟨58⟩	CH_3· + H·	→ CH_4		2.0×10^{14}	
⟨59⟩	C_3H_5· + H·	→ C_3H_6		2.0×10^{13}	
⟨60⟩	C_2H_3· + CH_3·	→ C_3H_6		1.0×10^{13}	
⟨61⟩	C_3H_5· + H·	→ C_3H_6		2.0×10^{13}	
⟨62⟩	CH_3· + CH_3·	→ C_2H_6		1.73×10^{13}	
⟨63⟩	CH_3· + CH_3·	→ C_2H_5· + H·		4.3×10^9	
⟨64⟩	CH_3· + CH_3·	→ $C_2H_4 + H_2$		2.87×10^{10}	

[a] For abbreviated structures see Appendix, Table A2.
[b] Pre-exponential factor.
[c] Rate constant.
[d] Activation energy.

Roscoe and Thompson added to the Chen and Back mechanism isomerization (as in reactions ⟨55⟩ and ⟨56⟩), propagation and termination reactions with reactants and radicals containing fewer than 3 carbon atoms. The mechanism of Roscoe and Thompson, with fitting of the kinetic gas constants, simulates the system at 1038 K under 433 torr and in a batch reactor. However, it is quite a different problem for the liquid products and coke.

Based on the Chen and Back mechanism, it seems interesting to try to complete and adapt the Roscoe and Thompson mechanism in such a way that the latter could explain the yields of heavier products (such as benzene) that appear at high reaction rates and long residence times. First, the system model of Roscoe and Thompson was compared with experimental results, using experimental conditions. This reaction system consists of 64 ERs (Table 2).

Concerning the simulated variations of H_2 C_2H_6, C_2H_4, C_2H_2 and C_3H_6 with reaction times, it can be shown that the simulated results obtained are not good enough and that the concentration of C_2H_4 stays less than those of C_2H_6 and that H_2 concentration is too low. This mechanism without addition of other ERs is not sufficient to explain the formation of products during the pyrolysis of methane in this study.

Mechanism taking account of C_4 products

Formation of H_2, C_2H_4, C_2H_6, C_2H_2 and C_3H_6

Before explaining the mechanism, and for brevity, the final mechanism is presented in the Appendix (Table A1).

Mechanistic modeling started with the basic set of ERs used in earlier work for the prediction of product formation and all the ERs with rates

parameters known in the literature. The rate parameters have been found in the literature (Baulch [6], Zanthoff and Baerns [7], Tsang and Hampson [8] and Roscoe and Thompson [4]); in Table 3 the respective calculated rate constants are given. These values show that some rate parameters are in good agreement whereas others vary by several orders of magnitude. For that reason, these rate parameters can be modified within reasonable limits.

This model consists of 111 elementary reactions. Without changing the values of the parameters of mechanism 1, the simulated results show that H_2 concentration increases too rapidly compared to C_2H_6 and C_2H_4. The C_2H_4 concentration becomes higher than C_2H_6 at very low total concentrations. The C_2H_2 concentration was too high at low residence times.

Because the concentrations c_j and the reaction rate constants k_i of elementary reaction i can vary by several orders of magnitude, it is more convenient to use the sensitivity analysis σ_{ij} previously defined [9, 10]. This sensitivity coefficient can be regarded as a measure of the kinetic significance of elementary reaction i for the production and reaction of a substance j with a concentration c_j.

With this sensitivity analysis the main reactions that have an influence on these compounds are (with the corresponding values found in the literature) given in Table 3. The set of parameters $k_1 = 2 \times 10^{-3}$, $k_9 = 2.6 \times 10^{13}$, $k_{14} = 1.6 \times 10^9$, $k_{16} = 0.7 \times 10^{10}$, $k_{24} = 7.5$, $k_{46} = 8 \times 10^{-4}$, $k_{49} = 201.25$, $k_{51} = 0.156$, $k_{84} = 0.6$ and $k_{23} = 0.12$, with the adapted mechanism of Table 2 and the previous model, gives C_2H_4, H_2 and C_2H_6

TABLE 3

Rate parameters of ER compiled from several sources

ER No.	ER [a]		Rate constant
⟨1⟩	CH_4	$\rightarrow CH_3\cdot + H\cdot$	$8 \times 10^{-4} < k_1 < 4.26 \times 10^{-3}$
⟨9⟩	$2CH_3\cdot$	$\rightarrow C_2H_6$	$10^{13} < k_9 < 2.10^{13}$
⟨23⟩	C_2H_6	$\rightarrow C_2H_5\cdot + H\cdot$	$0.12 < k_{23} < 444$
⟨51⟩	C_2H_4	$\rightarrow C_2H_3\cdot + M\cdot$	$0.196 < k_{51} < 1.96$
⟨16⟩	$CH_3\cdot + C_2H_4$	$\rightarrow$ 'iC_3H_7'	$1.1 \times 10^{10} < k_{16}\ 1.54 \times 10^{10}$
⟨22⟩	$CH_3\cdot + C_2H_2$	$\rightarrow C_3H_5\cdot$	1.55×10^8
⟨24⟩	C_2H_6	$\rightarrow 2CH_3\cdot$	$7.5 < k_{24} < 19.9$
⟨52⟩	$C_2H_4 + CH_3\cdot$	$\rightarrow$ '$nC_3H_7\cdot$'	$1.1 \times 10^{10} < k_{52} < 1.54 \times 10^{10}$
⟨77⟩	'$iC_3H_7\cdot$'	$\rightarrow CH_3\cdot + C_2H_4$	$3.9 \times 10^8 < k_{77} < 4.6 \times 10^{10}$
⟨78⟩	'$iC_3H_7\cdot$'	$\rightarrow C_3H_6 + H\cdot$	$3.4 \times 10^6 < k_{78} < 4.2 \times 10^9$
⟨14⟩	$CH_3\cdot + C_2H_4$	$\rightarrow CH_4 + C_2H_3\cdot$	$1.6 \times 10^{10} < k_{14} < 4.9 \times 10^{10}$
⟨46⟩	C_2H_4	$\rightarrow C_2H_2 + H_2$	$0.08 < k_{46} < 2 \times 10^3$
⟨84⟩	C_3H_6	$\rightarrow CH_3\cdot + C_2H_3\cdot$	$0.6 < k_{84} < 1.6$

[a] For abbreviated structures see Appendix, Table A2.

concentrations in good agreement with the experimental values of concentrations except for the C_3H_6 concentration, which is always too high, but the fact that not all the reactions consuming C_3H_6 are written has to be taken into account.

Formation of CH_2=C=CH_2 (a-C_3H_4) and CH_3–C≡CH (p-C_3H_4) and C_4H_6

A sensitivity analysis for these two products was made. The reactions that modify only the concentrations of C_3H_4 are as follows.

For a-C_3H_4

$\langle 5 \rangle$ $CH_4 + C_3H_5\cdot \rightarrow CH_3\cdot + C_3H_6$

$\langle 87 \rangle$ $C_3H_6 \rightarrow C_3H_5\cdot + H\cdot$

$\langle 89 \rangle$ $C_3H_6 + H\cdot \rightarrow H_2 + \text{'}C_3H_5\text{'}$

$\langle 97 \rangle$ $C_3H_5\cdot \rightarrow \text{'}a\text{-}C_3H_4\text{'} + H\cdot$

For p-C_3H_4

$\langle 91 \rangle$ $C_3H_6 + CH_3\cdot \rightarrow CH_4 + \text{'}C_3H_5\text{'}$

$\langle 100 \rangle$ $\text{'}C_3H_5\cdot\text{'} \rightarrow \text{'}p\text{-}C_3H_4\text{'} + H\cdot$

$\langle 101 \rangle$ $\text{'}C_3H_5\cdot\text{'} \rightarrow C_2H_2 + CH_3\cdot$

The best values that fit our results are $a_{d,97} = 8.9 \times 10^{13}$, $k_{100} = 7.55 \times 10^6$, $a_{d,101} = 1.58 \times 10^{11}$, $k_{91} = 8.1 \times 10^9$. To make the simulated concentration of a-C_3H_4 too low, three reactions leading to this product were added as follows.

$\langle 114 \rangle$ $C_2H_3\cdot + C_2H_4 \rightarrow CH_3\cdot + a\text{-}C_3H_4$ $\quad k_d = 5.91 \times 10^7$

$\langle 115 \rangle$ $CH_3\cdot + C_3H_5\cdot \rightarrow CH_4 + a\text{-}C_3H_4$ $\quad k_d = 1 \times 10^{12}$

$\langle 116 \rangle$ $C_3H_5\cdot + C_3H_5\cdot \rightarrow C_3H_6 + a\text{-}C_3H_4$ $\quad k_d = 1 \times 10^{12}$

To decrease p-C_3H_4 concentration three reactions with p-C_3H_4 were added [11] and to increase the concentration of p-C_3H_4 the ERs

$\langle 112 \rangle$ $C_3H_5\cdot \rightarrow H\cdot + p\text{-}C_3H_4$ $\quad k_d = 6.7$

$\langle 118 \rangle$ $H\cdot + p\text{-}C_3H_4 \rightarrow C_3H_5\cdot$ $\quad k_d = 7.48 \times 10^{11}$

$\langle 119 \rangle$ $p\text{-}C_3H_4 + H\cdot \rightarrow CH_3\cdot + C_2H_2$ $\quad k_d = 7.22 \times 10^{11}$

were included, and a mass sensitivity analysis with the more complete mechanism was made. The only two reactions important for a-C_3H_4 formation are

$\langle 87 \rangle$ $C_3H_6 \rightarrow C_3H_5\cdot + H\cdot$

$\langle 97 \rangle$ $C_3H_5\cdot \rightarrow a\text{-}C_3H_4 + H\cdot$

with $k_{87} = 2$, $a_{d,97} = 2 \times 10^{14}$, $k_1 = 1.7 \times 10^3$ (to decrease the conversion), $k_{100} = 1.25 \times 10^5$ (to decrease the concentration of p-C_3H_4).

With the proposed parameters, C_4H_6 concentrations do not exceed 0.65×10^{-15} mol cm^{-3}.

Reactions that have a real influence on C_4H_6 formation are

$\langle 54 \rangle$ $C_2H_3 \rightarrow C_2H_2 + H\cdot$

$\langle 64 \rangle$ $C_2H_3\cdot + C_2H_4 \rightarrow C_4H_6 + H\cdot$

$\langle 67 \rangle$ $C_2H_2 + H\cdot \rightarrow C_2H_3\cdot$

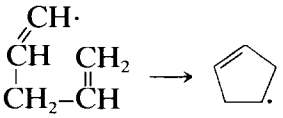
The best fit between experimental and simulated results was obtained with $k_{54} = 5 \times 10^8$ and $k_6 = 10^{11}$.

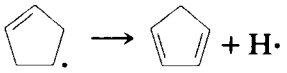
The mechanism obtained with all these modifications consists of 119 reactions (ERs $\langle 1 \rangle$–$\langle 119 \rangle$ of Table A1 in the Appendix).

C_5H_6 and C_6H_6 formations

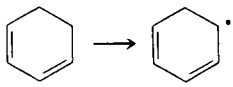
C_5H_6 formation [11]. A formation scheme for C_5H_6 could be

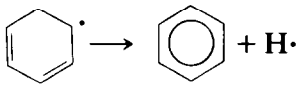
$CH_2{=}CH{-}\dot{C}H_2 + CH{\equiv}CH \longrightarrow CH_2{=}CH{-}CH_2{-}CH{=}\dot{C}H$





Benzene formation. Three ways of forming benzene were considered. With the same scheme as for C_5H_6, the following reactions were added.

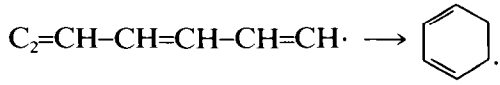


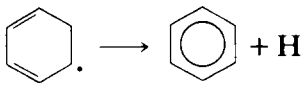


From $C_2H_3\cdot$ and C_2H_2 [12], the main reactions are

$CH_2{=}CH\cdot + CH{\equiv}CH \rightarrow CH_2{=}CH{-}CH{=}CH\cdot$

$CH_2{=}CH{-}CH{=}CH\cdot + CH{\equiv}CH \rightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH\cdot$





From the $CH_3\cdot$ radical and C_2H_2 [12], the main reactions are

$$CH{\equiv}CH + CH_3\cdot \rightarrow CH_3{-}CH{=}CH\cdot$$

$$CH_3{-}CH{=}CH\cdot \rightarrow \cdot CH_2{-}CH{=}CH_2$$

$$\cdot CH_2{-}CH{=}CH_2 + \cdot CH_2{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH$$

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + H\cdot \rightarrow \cdot CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2 + H_2$$

$$\cdot CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \longrightarrow \text{  } + H\cdot$$

$$\text{  } + H\cdot \longrightarrow \text{  } + H_2$$

$$\text{  } \longrightarrow \text{  } + H\cdot$$

These reactions are added to the previous mechanism.

Simulation. To check the parameters with most influence, a sensitivity analysis on the complete mechanism was made. The reactions that have an influence on C_5H_6 and C_6H_6 are

$\langle 127 \rangle$ $C_3H_5\cdot + C_2H_2 \rightarrow C_5H_7\cdot$

$\langle 128 \rangle$ $C_3H_5\cdot + C_2H_2 \rightarrow C_5H_6 + H\cdot$

$\langle 131 \rangle$ $C_3H_5\cdot + C_2H_3 \rightarrow$ '$C_5H_7\cdot$'

$\langle 143 \rangle$ $C_5H_5\cdot + H\cdot \rightarrow C_5H_6$

$\langle 146 \rangle$ $C_5H_6 \rightarrow C_5H_5\cdot + H\cdot$

$\langle 159 \rangle$ $C_6H_8 \rightarrow CH_3\cdot + C_5H_5\cdot$

$\langle 161 \rangle$ $C_6H_8 \rightarrow C_6H_7\cdot + H\cdot$

However, the new reactions added to the treatment of C_5H_6 and C_6H_6 lead to changes in the concentrations of C_6H_6, C_2H_2 and p-C_3H_4. By the sensitivity analysis, it is shown that $\langle 5 \rangle$, $\langle 84 \rangle$ and $\langle 87 \rangle$ improve the results. The reactions that only have an influence on C_4H_6 were $\langle 175 \rangle$ and $\langle 182 \rangle$.

The final rate constants were found to be $k_{127} = 7.48 \times 10^{11}$, $k_{128} = 8.68 \times 10^{11}$, $k_{131} = 2.21 \times 10^{11}$, $k_5 = 0.5 \times 10^{10}$, $k_{84} = 3.5$, $k_{168} = 0.5 \times 10^7$, $k_{113} = 1 \times 10^9$, $k_{120} = 1 \times 10^{11}$, $k_{87} = 3$, $k_1 = 1.6 \times 10^{-3}$, $a_{d,97} = 4 \times 10^{14}$, $k_{143} = 1 \times 10^{16}$, $a_{d,72} = 7 \times 10^{10}$, $k_{182} = 2 \times 10^{10}$ and $k_{175} = 4 \times 10^{11}$. The corresponding final mechanism is written in the Appendix.

TABLE 4

Final simulated product concentrations (10^{-6} mol l^{-1})

Molecule [a]	Time (s)													
	0.17	0.34	0.51	0.68	0.85	1.02	1.19	1.36	1.53	1.7	1.87	2.04	2.21	2.38
H_2	2.06	4.94	8.61	13.02	18.21	24.21	31.10	38.97	47.93	58.10	69.64	82.73	97.58	114.4
C_2H_6	1.45	2.55	3.36	3.99	4.50	4.94	5.35	5.74	6.14	6.54	6.95	7.39	7.86	8.35
C_2H_4	0.28	1.09	2.27	3.72	5.34	7.09	8.96	10.93	13.02	15.23	17.60	20.14	22.91	25.96
C_3H_6	–	0.03	0.10	0.21	0.39	0.61	0.89	1.24	1.64	2.12	2.66	3.29	4.02	4.85
C_2H_2	–	0.03	0.09	0.20	0.36	0.57	0.82	1.11	1.43	1.79	2.18	2.59	3.04	3.51
C_4H_6	–	–	–	–	0.01	0.02	0.04	0.06	0.09	0.13	0.19	0.25	0.33	0.42
a-C_3H_4	–	–	0.02	0.04	0.09	0.15	0.23	0.33	0.44	0.56	0.68	0.81	0.94	1.07
p-C_3H_4	–	–	0.01	0.03	0.08	0.17	0.31	0.51	0.78	1.11	1.50	1.92	2.37	2.80
C_5H_6	–	–	–	–	–	–	–	0.01	0.02	0.04	0.06	0.11	0.17	0.26
C_6H_6	–	–	–	–	–	–	0.02	0.04	0.07	0.13	0.22	0.36	0.55	0.81

[a] For abbreviated structures see Appendix, Table A2.

With the hypothesis of a good fit between the experimental and theoretical conversions of methane, Table 4 resumes the concentration values that can be compared with the experimental data (cf. Table 1). Figure 2 shows good agreement between experimental concentrations and concentrations calculated by the simulation model, as functions of residence time.

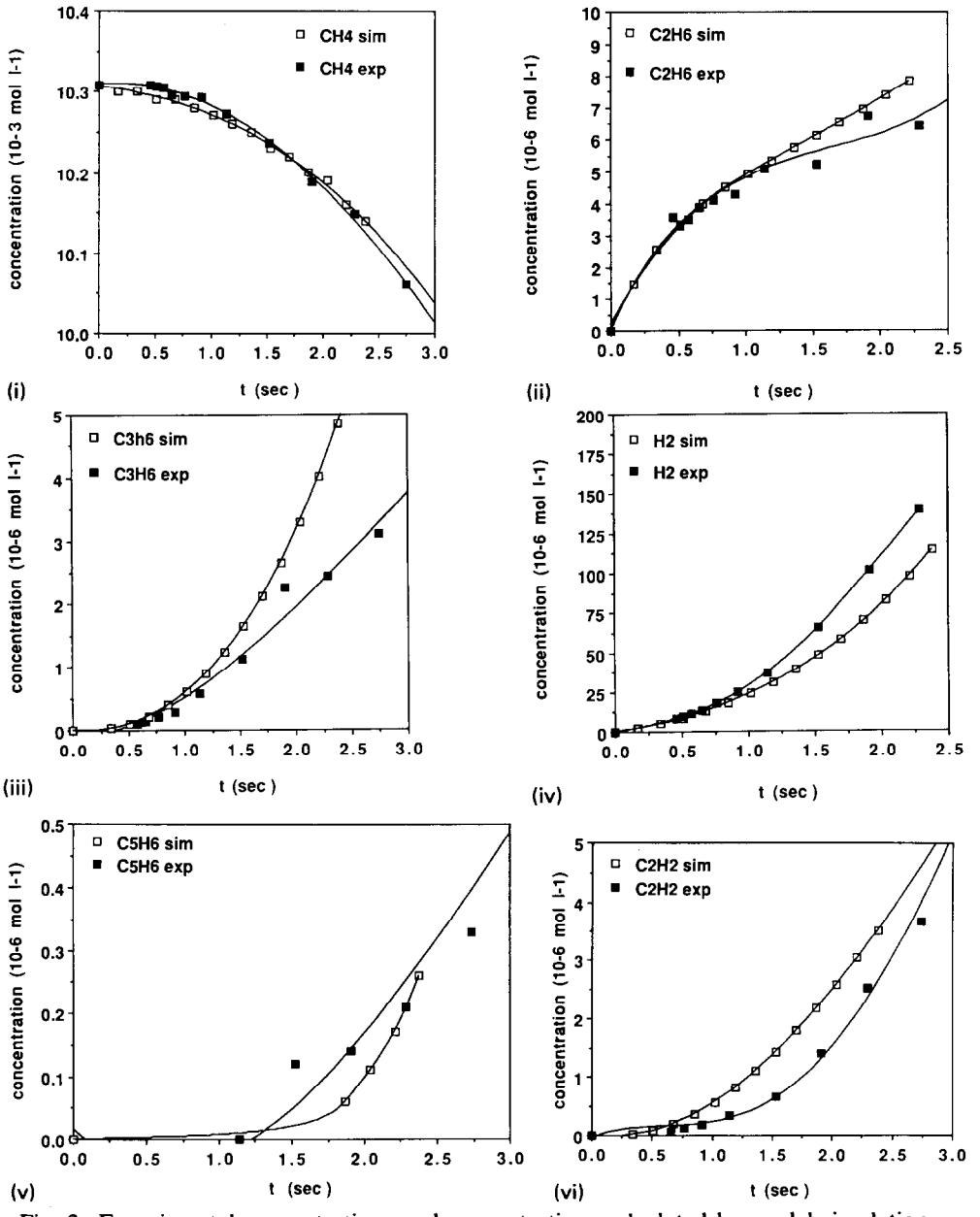
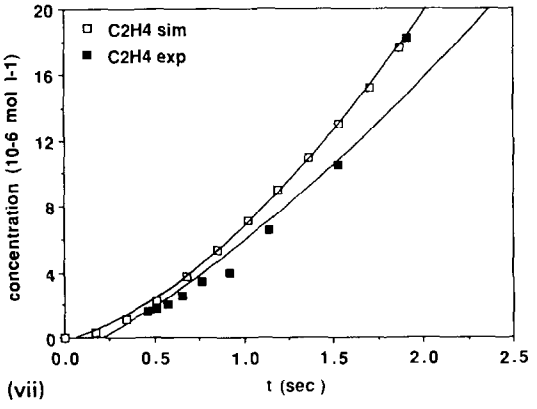
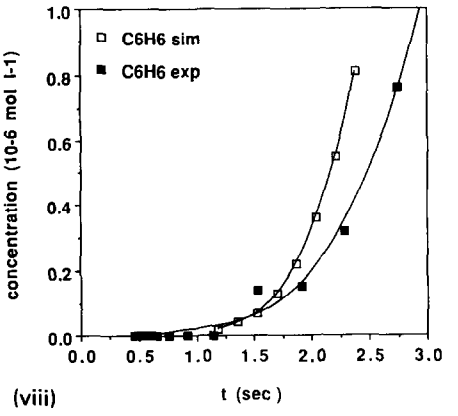
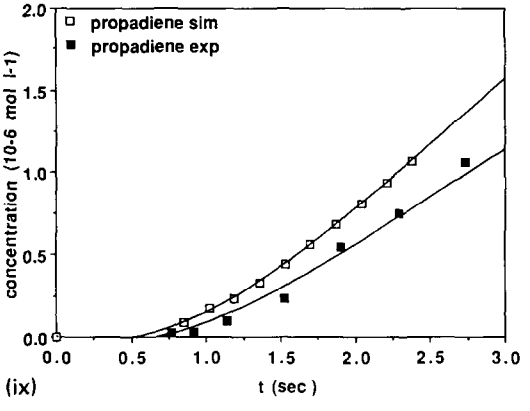
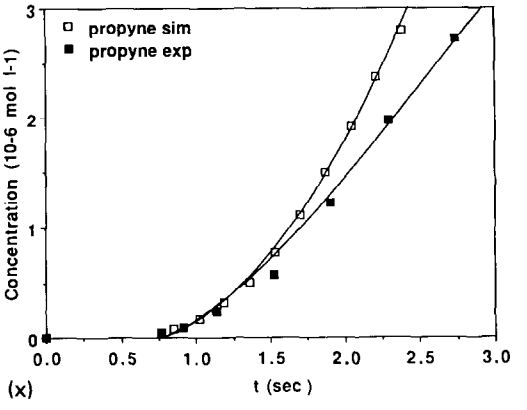


Fig. 2. Experimental concentrations and concentrations calculated by model simulations, as function of residence time.









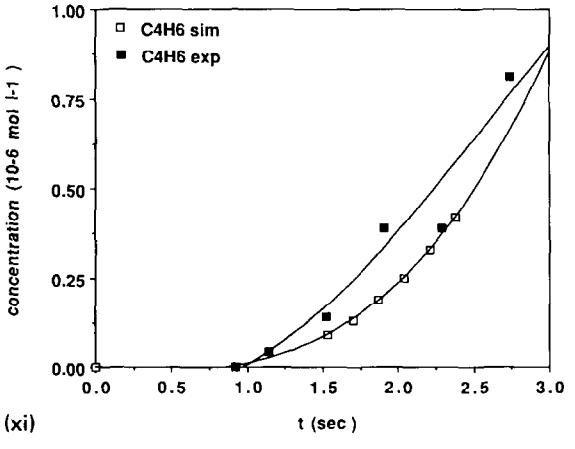


Fig. 2. (continued)

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APPENDIX

TABLE A1

The final mechanism

ER No.	ER [a]		k_d [b]	a_d [c]	e_d [d]
Reactions with CH_4					
⟨1⟩	CH_4	$\rightarrow CH_3\cdot + H\cdot$	1.6×10^{-3}		
⟨2⟩	$CH_4 + H\cdot$	$\rightarrow CH_3\cdot + H_2$	6.63×10^{11}		
⟨3⟩	$CH_4 + C_2H_5\cdot$	$\rightarrow CH_3\cdot + C_2H_6$	2.07×10^{8}		
⟨4⟩	$CH_4 + C_2H_3\cdot$	$\rightarrow CH_3\cdot + C_2H_4$	1.72×10^{9}		
⟨5⟩	$CH_4 + C_3H_5\cdot$	$\rightarrow CH_3\cdot + C_3H_6$	0.5×10^{10}		
⟨6⟩	$CH_4 + $ 'i-$C_3H_7\cdot$'	$\rightarrow CH_3\cdot + C_3H_8$	5.05×10^{8}		

TABLE A1 (continued)

ER No.	ER [a]		k_d [b]	a_d [c]	e_d [d]
Reactions with CH_3·					
⟨7⟩	$CH_3· + H_2$	$\rightarrow CH_4 + H·$	5.29×10^{10}		
⟨8⟩	$CH_3· + H·$	$\rightarrow CH_4$	3.77×10^{12}		
⟨9⟩	$CH_3· + CH_3·$	$\rightarrow C_2H_6$	2.6×10^{13}		
⟨10⟩	$CH_3· + CH_3·$	$\rightarrow C_2H_4 + H_2$	2.5×10^{10}		
⟨11⟩	$CH_3· + CH_3·$	$\rightarrow C_2H_5· + H·$	4.3×10^{9}		
⟨12⟩	$CH_3· + C_2H_6$	$\rightarrow CH_4 + C_2H_5·$	6.47×10^{10}		
⟨13⟩	$CH_3· + C_2H_5·$	$\rightarrow CH_4 + C_2H_4$	6×10^{11}		
⟨14⟩	$CH_3· + C_2H_4$	$\rightarrow CH_4 + C_2H_3·$	1.6×10^{9}		
⟨15⟩	$CH_3· + C_2H_3·$	$\rightarrow CH_4 + C_2H_2$	3.9×10^{11}		
⟨16⟩	$CH_3· + C_2H_4$	$\rightarrow$ '*i*-C_3H_7·'	0.7×10^{10}		
⟨17⟩	$CH_3· + C_2H_5·$	$\rightarrow C_3H_8$	1.38×10^{13}		
⟨18⟩	$CH_3· + C_2H_4·$	$\rightarrow C_3H_6$	1×10^{13}		
⟨19⟩	$CH_3· + C_3H_8$	$\rightarrow CH_4 +$ '*i*-C_3H_7·'	2.6×10^{10}		
⟨20⟩	$CH_3· + C_3H_8$	$\rightarrow CH_4 +$ '*n*-C_3H_7·'	2.6×10^{10}		
⟨21⟩	$CH_3· + C_3H_6$	$\rightarrow CH_4 + C_3H_5·$	3.3×10^{9}		
⟨22⟩	$CH_3· + C_2H_2$	$\rightarrow C_3H_5·$	2.7×10^{10}		
Reactions with C_2H_6					
⟨23⟩	C_2H_6	$\rightarrow C_2H_5· + H·$	1.2		
⟨24⟩	C_2H_6	$\rightarrow CH_3· + CH_3·$	7.5		
⟨25⟩	$C_2H_6 + H·$	$\rightarrow C_2H_5· + H_2$	4.35×10^{12}		
⟨26⟩	$C_2H_6 + C_2H_3·$	$\rightarrow C_2H_5· + C_2H_4$	1.7×10^{9}		
⟨27⟩	$C_2H_6 + C_3H_5·$	$\rightarrow C_2H_5· + C_3H_6$	1×10^{9}		
⟨28⟩	C_2H_6 + '*i*-C_3H_7·'	$\rightarrow C_2H_5· + C_3H_8$	1.78×10^{9}		
⟨29⟩	C_2H_6 + '*n*-C_3H_7·'	$\rightarrow C_2H_5· + C_3H_8$	1.87×10^{9}		
⟨30⟩	$C_2H_5·$	$\rightarrow C_2H_4 + H·$	3.9×10^{6}		
⟨31⟩	$C_2H_5· + H·$	$\rightarrow C_2H_4 + H_2$	2.6×10^{12}		
⟨32⟩	$C_2H_5· + H·$	$\rightarrow CH_3· + CH_3·$	3.3×10^{13}		
⟨33⟩	$C_2H_5· + H·$	$\rightarrow C_2H_6$	3.6×10^{13}		
⟨34⟩	$C_2H_5· + H_2$	$\rightarrow C_2H_6 + H·$	1.5×10^{10}		
⟨35⟩	$C_2H_5· + C_2H_5·$	$\rightarrow C_2H_6 + C_2H_4$	1.4×10^{12}		
⟨36⟩	$C_2H_5· + C_2H_3·$	$\rightarrow C_2H_4 + C_2H_4$	2.8×10^{11}		
⟨37⟩	$C_2H_5· + C_3H_5·$	$\rightarrow C_2H_4 + C_3H_6$	3.98×10^{11}		
⟨38⟩	$C_2H_5· + C_3H_8$	$\rightarrow C_2H_6$ + '*i*-C_3H_7·'	1.26×10^{10}		
⟨39⟩	$C_2H_5· + C_3H_8$	$\rightarrow C_2H_6$ + '*n*-C_3H_7·'	1.26×10^{10}		
⟨40⟩	$C_2H_5· + C_2H_5·$	$\rightarrow C_4H_{10}$	1×10^{13}		
Reactions with C_2H_4					
⟨41⟩	$C_2H_4 + H·$	$\rightarrow C_2H_5·$	5.5×10^{12}		
⟨42⟩	$C_2H_4 + H·$	$\rightarrow C_2H_3· + H_2$	5.28×10^{10}		
⟨43⟩	$C_2H_4 + C_3H_5·$	$\rightarrow C_2H_3· + C_3H_6$	2.43×10^{9}		
⟨44⟩	C_2H_4 + '*i*-C_3H_7·'	$\rightarrow C_2H_3· + C_3H_8$	2.53×10^{8}		
⟨45⟩	C_2H_4 + '*n*-C_3H_7·'	$\rightarrow C_2H_3· + C_3H_8$	2.53×10^{8}		
⟨46⟩	C_2H_4	$\rightarrow C_2H_2 + H_2$	8×10^{-4}		
⟨47⟩	$C_2H_4 + H_2$	$\rightarrow C_2H_5· + H·$	16.44		
⟨48⟩	$C_2H_4 + C_2H_5·$	$\rightarrow C_2H_6 + C_2H_3·$	3.2		
⟨49⟩	$C_2H_4 + C_2H_4$	$\rightarrow C_2H_3· + C_2H_5·$	201.25		
⟨50⟩	$C_2H_4 + C_2H_2$	$\rightarrow C_2H_3· + C_2H_3·$	35.73		
⟨51⟩	C_2H_4	$\rightarrow C_2H_3· + H·$	0.196		
⟨52⟩	$C_2H_4 + CH_3·$	$\rightarrow$ '*n*-C_3H_7·'		1.26×10^{11}	7.71×10^{3}
⟨53⟩	$C_2H_4 + C_2H_5·$	$\rightarrow$ '*p*-C_4H_9·'		6.31×10^{10}	7.59×10^{3}

TABLE A1 (continued)

ER No.	ER [a]		k_d [b]	a_d [c]	e_d [d]
Reactions with C_2H_3·					
⟨54⟩	C_2H_3·	→ $C_2H_2 + H$·	5×10^8		
⟨55⟩	C_2H_3· + H·	→ $C_2H_2 + H_2$	3.7×10^{13}		
⟨56⟩	C_2H_3· + H_2	→ C_2H_4 + H·	2.6×10^{11}		
⟨57⟩	C_2H_3· + C_2H_3·	→ $C_2H_4 + C_2H_2$	9.64×10^{11}		
⟨58⟩	C_2H_3· + H·	→ C_2H_4	1×10^{13}		
⟨59⟩	C_2H_3· + C_2H_6	→ $C_2H_4 + C_2H_5$·	9.75×10^9		
⟨60⟩	C_2H_3· + CH_3·	→ C_3H_5· + H·	1.83×10^{12}		
⟨61⟩	C_2H_3· + C_2H_5·	→ '*i*-C_4H_8'	2.2×10^{12}		
⟨62⟩	C_2H_3· + C_2H_5·	→ C_3H_5· + CH_3·	1.28×10^{13}		
⟨63⟩	C_2H_3· + C_2H_5·	→ $C_2H_2 + C_2H_6$	4.82×10^{11}		
⟨64⟩	C_2H_3· + C_2H_4	→ 'C_4H_6' + H·	1×10^{11}		
⟨65⟩	C_2H_3· + C_2H_3·	→ 'C_4H_6'	9.27×10^{12}		
⟨66⟩	C_2H_3· + C_2H_3·	→ C_4H_5· + H·	3.64×10^{11}		
Reactions with C_2H_2					
⟨67⟩	C_2H_2 + H·	→ C_2H_3·	7.7×10^{12}		
⟨68⟩	C_2H_2 + H_2	→ C_2H_3· + H·	13.7		
⟨69⟩	C_2H_2 + H_2	→ C_2H_4	4.9×10^4		
⟨70⟩	C_2H_2	→ C_2H· + H·	4.51×10^{-3}		
⟨71⟩	C_2H_2 + CH_3·	→ CH_4 + C_2H·	1.55×10^8		
⟨72⟩	C_2H_2 + CH_3·	→ 'C_3H_5·'		7×10^{10}	7.67×10^2
Reaction with C_2H·					
⟨73⟩	C_2H· + H·	→ C_2H_2	6.26×10^{19}		
Reactions with C_3H_8					
⟨74⟩	C_3H_8	→ CH_3· + C_2H_5·	4.75×10^4		
⟨75⟩	C_3H_8 + H·	→ '*i*-C_3H_7·' + H_2	3×10^{12}		
⟨76⟩	C_3H_8 + H·	→ '*n*-C_3H_7·' + H_2	3×10^{12}		
Reactions with C_3H_7					
⟨77⟩	'*i*-C_3H_7·'	→ CH_3· + C_2H_4	4.58×10^9		
⟨78⟩	'*i*-C_3H_7·'	→ C_3H_6 + H·	4.19×10^{10}		
⟨79⟩	'*i*-C_3H_7·' + H·	→ C_3H_8	2×10^{13}		
⟨80⟩	'*i*-C_3H_7·' + '*i*-C_3H_7·'	→ $C_3H_6 + C_3H_8$	2.4×10^{12}		
⟨81⟩	'*n*-C_3H_7·' + '*n*-C_3H_7·'	→ $C_3H_6 + C_3H_8$	1.6×10^{12}		
⟨82⟩	'*n*-C_3H_7·'	→ CH_3· + C_2H_4	4.58×10^9		
⟨83⟩	'*n*-C_3H_7·'	→ C_3H_6 + H·	4.19×10^9		
Reactions with C_3H_6					
⟨84⟩	C_3H_6	→ CH_3· + C_2H_3·	3.5		
⟨85⟩	C_3H_6 + H·	→ '*i*-C_3H_7·'	2.66×10^{12}		
⟨86⟩	C_3H_6 + H·	→ '*n*-C_3H_7·'	1.38×10^{13}		
⟨87⟩	C_3H_6	→ C_3H_5· + H·	3		
⟨88⟩	C_3H_6	→ 'C_3H_5·' + H·	0.104×10^{-3}		
⟨89⟩	C_3H_6 + H·	→ $H_2 + C_3H_5$·	0.25×10^{14}		
⟨90⟩	C_3H_6 + H·	→ H_2 + 'C_3H_5·'	2×10^{10}		
⟨91⟩	C_3H_6 + CH_3·	→ CH_4 + 'C_3H_5·'	8.1×10^9		
⟨92⟩	C_3H_6 + C_2H_5·	→ $C_2H_6 + C_3H_5$·	3.34×10^9		
⟨93⟩	C_3H_6 + C_2H_5·	→ C_2H_6 + 'C_3H_5·'	1×10^9		
⟨94⟩	C_3H_6 + CH_3·	→ '*i*-C_4H_9·'		3.16×10^{11}	7.39×10^3

TABLE A1 (continued)

ER No.	ER [a]		k_d [b]	a_d [c]	e_d [d]
Reactions with C_3H_5·					
⟨95⟩	C_3H_5· + H·	→ C_3H_6	2×10^{13}		
⟨96⟩	C_3H_5· + H_2	→ C_3H_6 + H·	3.4×10^{11}		
⟨97⟩	C_3H_5·	→ '*a*-C_3H_4' + H·		4×10^{14}	5.9×10^{4}
⟨98⟩	'C_3H_5·' + CH_4	→ C_3H_6 + CH_3·	0.27×10^{9}		
⟨99⟩	'C_3H_5·' + C_2H_6	→ C_3H_6 + C_2H_5·	4×10^{8}		
⟨100⟩	'C_3H_5·'	→ '*p*-C_3H_4' + H·	1.25×10^{5}		
⟨101⟩	'C_3H_5·'	→ C_2H_2 + CH_3·		1.58×10^{11}	3.76×10^{4}
Reactions with C_3H_4					
⟨102⟩	'*p*-C_3H_4' + H·	→ 'C_3H_5·'		3.47×10^{13}	1.987×10^{3}
⟨103⟩	'*a*-C_3H_4' + H·	→ C_3H_5·		3.47×10^{13}	1.987×10^{3}
Reactions with C_4H_9					
⟨104⟩	'*i*-C_4H_9·'	→ '*i*-C_4H_8' + H·		2×10^{13}	4.03×10^{4}
⟨105⟩	'*i*-C_4H_9·'	→ C_3H_6 + CH_3·		2×10^{14}	3.32×10^{4}
⟨106⟩	'*p*-C_4H_9·'	→ '*i*-C_4H_8' + H·		1.26×10^{13}	3.85×10^{4}
⟨107⟩	'*p*-C_4H_9·'	→ C_2H_4 + C_2H_5·		2.51×10^{13}	2.88×10^{4}
⟨108⟩	'*p*-C_4H_9·'	→ C_3H_6 + CH_3·		1.25×10^{12}	2.16×10^{4}
Reactions with C_4H_8					
⟨109⟩	'*i*-C_4H_8' + H·	→ '*i*-C_4H_9·'		8.94×10^{12}	1.2×10^{3}
Reactions with C_3H_7					
⟨110⟩	'*n*-C_3H_7'	→ '*i*-C_3H_7·'		2.51×10^{12}	3.4×10^{4}
⟨111⟩	'*i*-C_3H_7·'	→ '*n*-C_3H_7·'		1×10^{13}	3.795×10^{4}
⟨112⟩	C_3H_5·	→ H· + '*p*-C_3H_4'	6.7		
⟨113⟩	CH_3· + C_2H_2	→ '*p*-C_3H_4' + H·	1×10^{9}		
⟨114⟩	C_2H_3 + C_2H_4	→ CH_3· + '*a*-C_3H_4'	5.91×10^{7}		
⟨115⟩	CH_3· + C_3H_5·	→ CH_4 + '*a*-C_3H_4'	1×10^{12}		
⟨116⟩	C_3H_5· + C_3H_5·	→ C_3H_6 + '*a*-C_3H_4'	1×10^{12}		
⟨117⟩	H· + '*p*-C_3H_4'	→ C_3H_5·	7.48×10^{11}		
⟨118⟩	'*p*-C_3H_4' + H·	→ CH_3· + C_2H_2	7.22×10^{11}		
C_5H_6 formation					
⟨119⟩	CH_3· + C_2H_4	→ C_3H_6 + H·	9.22×10^{8}		
⟨120⟩	CH_3· + '*a*-C_3H_4'	→ C_3H_3· + CH_4	1×10^{11}		
⟨121⟩	CH_3· + '*p*-C_3H_4'	→ C_3H_3· + CH_4	1.05×10^{10}		
⟨122⟩	CH_3· + C_5H_5·	→ C_6H_8	2.29×10^{12}		
⟨123⟩	CH_3· + C_5H_5·	→ C_6H_7· + H·	6.55×10^{9}		
⟨124⟩	CH_3· + C_5H_6	→ CH_4 + C_5H_5·	3.475×10^{10}		
⟨125⟩	CH_3· + C_6H_8	→ C_6H_7· + CH_4	4.06×10^{10}		
⟨126⟩	C_2H_4 + CH_4	→ CH_3· + C_2H_5·	0.292		
⟨127⟩	C_3H_5· + C_2H_2	→ C_5H_7·	7.48×10^{11}		
⟨128⟩	C_3H_5· + C_2H_2	→ C_5H_6 + H·	8.68×10^{11}		
⟨129⟩	C_3H_5· + C_5H_5·	→ '*a*-C_3H_4' + C_5H_6	1×10^{12}		
⟨130⟩	C_3H_5· + C_5H_5·	→ '*p*-C_3H_4' + C_5H_6	1×10^{12}		
⟨131⟩	C_3H_5· + C_2H_2	→ 'C_5H_7·'	2.21×10^{11}		
⟨132⟩	C_3H_5·	→ CH_3· + C_2H_2	52.52		
⟨133⟩	'*p*-C_3H_4'	→ C_3H_3· + H·	0.185		
⟨134⟩	C_3H_3· + H·	→ '*p*-C_3H_4'	1.39×10^{17}		
⟨135⟩	C_3H_3· + CH_4	→ '*a*-C_3H_4' + CH_3·	1.93×10^{7}		

TABLE A1 (continued)

ER No.	ER [a]		k_d [b]	a_d [c]	e_d [d]
⟨136⟩	$C_3H_3\cdot + CH_4$	$\rightarrow$ 'p-C_3H_4' + $CH_3\cdot$	6.96×10^7		
⟨137⟩	$C_3H_6 + H\cdot$	$\rightarrow CH_3\cdot + C_2H_4$	2.82×10^{11}		
⟨138⟩	'a-C_3H_4' + C_3H_6	$\rightarrow C_3H_5\cdot + C_3H_5\cdot$	2.41×10^6		
⟨139⟩	'a-C_3H_4' + CH_4	$\rightarrow C_3H_5\cdot + CH_3\cdot$	3.57×10^3		
⟨140⟩	'a-C_3H_4' + C_5H_6	$\rightarrow C_3H_5\cdot + C_5H_5\cdot$	1.53×10^9		
⟨141⟩	'i-C_4H_8' + $H\cdot$	$\rightarrow CH_3\cdot + C_3H_6$	7.2×10^{12}		
⟨142⟩	$C_5H_5\cdot + C_5H_5\cdot$	$\rightarrow C_{10}H_8 + H_2$	1.95×10^9		
⟨143⟩	$C_5H_5\cdot + H\cdot$	$\rightarrow C_5H_6$	1×10^{16}		
⟨144⟩	$C_5H_5\cdot + H_2$	$\rightarrow C_5H_6 + H\cdot$	1.36×10^6		
⟨145⟩	$C_5H_5\cdot + CH_4$	$\rightarrow CH_3\cdot + C_5H_6$	8.15×10^4		
⟨146⟩	C_5H_6	$\rightarrow C_5H_5\cdot + H\cdot$	111.82		
⟨147⟩	$C_5H_6 + H\cdot$	$\rightarrow C_5H_5\cdot + H_2$	1.21×10^{13}		
⟨148⟩	$C_5H_6 + H\cdot$	$\rightarrow C_5H_7\cdot$	8.67×10^{13}		
⟨149⟩	$C_5H_6 + H\cdot$	$\rightarrow C_3H_5\cdot + C_2H_2$	9.21×10^{11}		
⟨150⟩	$C_5H_7\cdot$	$\rightarrow$ '$C_5H_7\cdot$'	1.52×10^7		
⟨151⟩	$C_5H_7\cdot$	$\rightarrow C_5H_6 + H\cdot$	1.19×10^7		
⟨152⟩	$C_5H_7\cdot$	$\rightarrow C_3H_5\cdot + C_2H_2$	1.08×10^5		
⟨153⟩	'$C_5H_7\cdot$'	$\rightarrow C_5H_7\cdot$	4.33×10^9		
⟨154⟩	'$C_5H_7\cdot$'	$\rightarrow C_3H_5\cdot + C_2H_2$	0.91×10^7		
⟨155⟩	$C_6H_6 + H\cdot$	$\rightarrow C_6H_7\cdot$	1.84×10^{13}		
⟨156⟩	$C_6H_7\cdot + H\cdot$	$\rightarrow CH_3\cdot + C_5H_5\cdot$	3.79×10^{14}		
⟨157⟩	$C_6H_7\cdot + H\cdot$	$\rightarrow C_6H_8$	6.33×10^{16}		
⟨158⟩	$C_6H_7\cdot + CH_4$	$\rightarrow C_6H_8 + CH_3\cdot$	2.77×10^5		
⟨159⟩	C_6H_8	$\rightarrow CH_3\cdot + C_5H_5\cdot$	171.2		
⟨160⟩	$C_{10}H_8 + H_2$	$\rightarrow C_5H_5\cdot + C_5H_5\cdot$	6.58×10^{-5}		
C_6H_6 formation					
⟨161⟩	C_6H_8	$\rightarrow C_6H_7\cdot + H\cdot$	81.57		
⟨162⟩	$C_6H_7\cdot$	$\rightarrow C_6H_6 + H\cdot$	2.09×10^8		
⟨163⟩	$C_2H_3\cdot + C_2H_2$	$\rightarrow$ '$C_4H_5\cdot$'	5.08×10^{10}		
⟨164⟩	'$C_4H_5\cdot$' + H_2	$\rightarrow$ 'C_4H_6' + $H\cdot$	8×10^9		
⟨165⟩	'$C_4H_5\cdot$' + CH_4	$\rightarrow$ 'C_4H_6' + $CH_3\cdot$	8×10^9		
⟨166⟩	'$C_4H_5\cdot$' + C_2H_2	$\rightarrow$ '$C_6H_7\cdot$'	5.08×10^{10}		
⟨167⟩	'$C_3H_5\cdot$' + H_2	$\rightarrow C_3H_6 + H\cdot$	3.5×10^{12}		
⟨168⟩	'$C_3H_5\cdot$'	$\rightarrow C_3H_5\cdot$	0.5×10^7		
⟨169⟩	$C_3H_5\cdot + C_3H_5\cdot$	$\rightarrow C_6H_{10}$	1.99×10^{13}		
⟨170⟩	$C_6H_{10} + H\cdot$	$\rightarrow$ '$C_6H_9\cdot$' + H_2	3.5×10^{12}		
⟨171⟩	$C_6H_{10} + CH_3\cdot$	$\rightarrow$ '$C_6H_9\cdot$' + CH_4	1.15×10^{10}		
⟨172⟩	'1-$C_6H_9\cdot$'	$\rightarrow$ '$C_6H_9\cdot$'	1.86×10^7		
⟨173⟩	$CH_3\cdot + C_3H_5\cdot$	$\rightarrow$ 'i-C_4H_8'	5.01×10^{13}		
⟨174⟩	'i-C_4H_8' + $H\cdot$	$\rightarrow$ '$C_4H_7\cdot$' + H_2	3.5×10^{12}		
⟨175⟩	'i-C_4H_8' + $CH_3\cdot$	$\rightarrow$ '$C_3H_7\cdot$' + CH_4	4×10^{11}		
⟨176⟩	$CH_3\cdot$ + '$C_4H_7\cdot$'	$\rightarrow$ 'C_5H_{10}'	2.51×10^{13}		
⟨177⟩	'C_5H_{10}' + $H\cdot$	$\rightarrow$ '2-$C_5H_9\cdot$' + H_2	3.5×10^{12}		
⟨178⟩	'C_5H_{10}' + $CH_3\cdot$	$\rightarrow$ '2-$C_5H_9\cdot$' + CH_4	1.15×10^{10}		
⟨179⟩	'2-$C_5H_9\cdot$'	$\rightarrow$ 'C_5H_8' + $H\cdot$	3.11×10^5		
⟨180⟩	'$C_4H_7\cdot$'	$\rightarrow$ 'C_4H_6' + $H\cdot$	1.56×10^5		
⟨181⟩	'C_4H_6' + $C_2H_3\cdot$	$\rightarrow$ '$C_6H_9\cdot$'	1.34×10^9		
⟨182⟩	'C_4H_6' + $CH_3\cdot$	$\rightarrow$ '1-$C_5H_9\cdot$'	2×10^{10}		
⟨183⟩	'1-$C_5H_9\cdot$'	$\rightarrow$ 'C_5H_8' + $H\cdot$	1.63×10^6		
⟨184⟩	'C_5H_8' + $H\cdot$	$\rightarrow$ '2-$C_5H_7\cdot$' + H_2	3.5×10^{12}		

TABLE A1 (continued)

ER No.	ER [a]		k_d [b]	a_d [c]	e_d [d]
⟨185⟩	'C_5H_8' + CH_3·	→ '2-C_5H_7·' + CH_4	1.15×10^{10}		
⟨186⟩	'2-C_5H_7·' + CH_3·	→ '1-C_6H_{10}'	5.01×10^{13}		
⟨187⟩	'C_6H_9·'	→ 'C_6H_8' + H·	1.4×10^{6}		
⟨188⟩	'C_6H_8'	→ C_6H_8	5.11×10^{6}		
⟨189⟩	C_6H_8 + H·	→ C_6H_7· + H_2	3.5×10^{12}		

[a] For abbreviated structures see Table A2.
[b] Rate constant.
[c] Pre-exponential factor (Arrhenius parameter).
[d] Activation energy (Arrhenius parameter).

TABLE A2

Abbreviated structures

Abbreviation	Structure
'C_3H_5·'	CH_3–CH=CH·
nC_3H_7	·CH_2–CH_2–CH_3
iC_3H_7	CH_3–CH·–CH_3
'*p*-C_3H_4'	CH_3–C≡CH (propyne)
'*a*-C_3H_4'	CH_2=C=CH_2 (propadiene)
'*i*-C_4H_9·'	CH_3–CH·–CH_2–CH_3
'*p*-C_4H_9·'	·CH_2–CH_2–CH_2–CH_3
'*i*-C_4H_8'	CH_2=CH–CH_2–CH_3
'*p*-C_4H_8'	CH_3–CH=CH–CH_3
'C_4H_5·'	CH_2=CH–CH=CH·
'C_4H_6'	CH_2=CH–CH=CH_2
'C_4H_7·'	CH_3–CH_2–C·=CH_2
'C_5H_7·'	CH_2=CH–CH_2–CH=CH·
'2-C_5H_7·'	CH_2=CH–CH=CH–CH_2·
'C_5H_8'	CH_3–CH=CH–CH=CH_2
'1-C_5H_9·'	CH_3–CH_2–CH·–CH=CH_2
'2-C_5H_9·'	CH_3–CH=C·–CH_2–CH_3
'C_5H_{10}'	CH_3–CH=CH–CH_2–CH_3
'C_6H_7·'	CH_2=CH–CH=CH–CH=CH·
'C_6H_8'	CH_2=CH–CH=CH–CH=CH_2
'1-C_6H_9·'	CH·=CH–CH_2–CH_2–CH=CH_2
'C_6H_9·'	CH_2=CH–CH_2–CH·–CH=CH_2
'C_6H_{10}'	CH_2=CH–CH_2–CH_2–CH=CH_2
'1-C_6H_{10}'	CH_3–CH_2–CH=CH–CH=CH_2
C_6H_7·	

TABLE A2 (continued)

Abbreviation	Structure
$C_5H_5\cdot$	
$C_5H_7\cdot$