Thermochimica Acta, 127 (1988) 247–258
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

KINETICS AND MECHANISM OF THE THERMAL CRACKING OF n-HEPTANE

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(Received 3 August 1987)

ABSTRACT

The kinetics and mechanism of the thermal decomposition of pure *n*-heptane at high conversions were investigated at temperatures of 660–780 ° C and reaction times of 0 40–1 02 s The conversion data were well represented by a first-order kinetic law with a pre-exponential factor of 5 88 × 10^{10} s^{-1} and an activation energy of 206 1 kJ mol^{-1} The inadequacy of the Rice–Kossiakoff theory in accounting satisfactorily for the formation of the products of n-heptane pyrolysis has been rationalized in terms of the secondary reactions of higher alpha-olefins

INTRODUCTION

Hydrocarbon pyrolysis is the key process for modern petrochemistry and will remain so in the future Production of ethylene has been a global business for about four decades [1] Many new pyrolysis plants have been constructed the world over and there is a wide range of feedstock flexibility [2,3] Presently, ethylene is quantitatively the most important chemical substance based on crude oil, and it is the base stock for 30% of all petrochemicals produced [4] Though technological and constructional improvements of hydrocarbon pyrolysis plants are high, knowledge of the mechanism of hydrocarbon pyrolysis is low This is due to the complex nature of pyrolysis reactions Research studies of the pyrolysis reactions of hydrocarbons, particularly alkanes, still continue, this is because minor technological improvements due, for example, to a better understanding of the mechanisms of hydrocarbon pyrolysis would be of great economic importance Most studies of hydrocarbon pyrolyses have been performed at low conversions (less than 600 ° C) and limited to light hydrocarbons [5–10] There are relatively few studies on the pyrolyses of high molecular weight hydrocarbons, some of these are on nonane [11], n-octane, iso-octane and C_6 branched alkanes [12], and n-heptane [18] The pyrolysis reactions of heavy hydrocarbons are so complex that the formation of the products cannot be explained satisfactorily by the Rice–Kossiakoff (R–K) free radical theory

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[14,15] On the other hand, the R–K theory accounts satisfactorily for the formation of products of the pyrolyses of light hydrocarbons at relatively mild conditions (500–650 °C) Pure n-heptane has been chosen as the reactant as it gives the highest conversion and yield of ethylene at 780 °C in the group C_5–C_{12} alkanes [13]

In this paper, we report on the kinetics and mechanism of the thermal decomposition of pure n-heptane at high conversions Detailed analysis of the pyrolysis products is necessary for the elucidation of the complex mechanism of n-heptane pyrolysis The adequacy of the R–K theory in explaining the formation of the products of n-heptane pyrolysis is also examined

EXPERIMENTAL

Materials

Pure n-heptane (99 7% purity, Hopkins and Williams, Essex, U K) was used as the pyrolysis feed Its purity was determined by the gas chromatograph (GC) High-purity nitrogen and hydrogen gases purchased from Industrial Gases Limited, Lagos, were used without further purification Liquid nitrogen was used for trapping products of coke-burnout

Instrumentation and procedure

The pyrolysis of n-heptane was carried out in an annular stainless steel reactor ($S/V = 16\ 3\ \text{cm}^{-1}$) with excessive nitrogen dilution at 1 atm pressure A detailed description of the experimental procedure has been given elsewhere [16]

Pulses of pure n-heptane (size, 2 0 μl) were injected into the system for a cracking run after the operating conditions have stabilized Experimental data were obtained over a wide range of conversions at temperatures of 660–780 °C and residence times of 0 40–1 02 s Detailed analysis of the products of n-heptane pyrolysis was carried out using three GCs on line, details of this analysis are shown in Table 1

RESULTS AND DISCUSSION

In presenting the results of this work the definitions of residence time, yield and selectivity used in previous studies [16,17] are adopted

Kinetic analysis

Pyrolyses of hydrocarbons may be represented fairly well by first-order kinetics [24] Besides, a first-order rate law was reported in earlier studies on

TABLE 1

Analysis of the products of *n*-heptane pyrolysis

	Carle GC TCD	Carle GC FID	Hitachi GC FID
Products analysed	H_2, CO and CO_2	C_1–C_4 Hydrocarbons	Lumped gas (C_1–C_4) peak and C_5 +
Column	5 Å Molecular sieve	Modified alumina	Squalane-on-chromosorb P 80/100 Mesh
Carrier gas	N_2	N_2	N_2
Column temp (° C)	60	60–70	100

n-heptane pyrolysis [18,25] Consequently, first-order kinetics was assumed in this work

$$-\ln(1-x)=k\tau$$

Figures 1 and 2 show the first-order plots of n-heptane pyrolysis, rate constants were estimated graphically from these plots and used in making the Arrhenius plots (Fig 3) The apparent kinetic rate parameters estimated for thermal decomposition of n-heptane are activation energy = 206 1 kJ mol^{-1} and pre-exponential factor = $5\ 88\times10^{10}$ s^{-1} Table 2 shows the comparison of kinetic rate parameters derived in this work with those reported previously in the literature

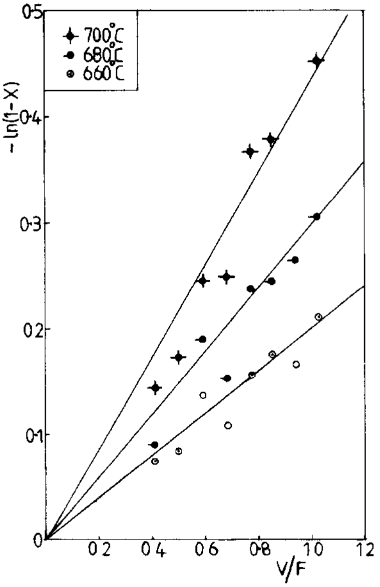


Fig 1 First-order plots of heptane pyrolysis

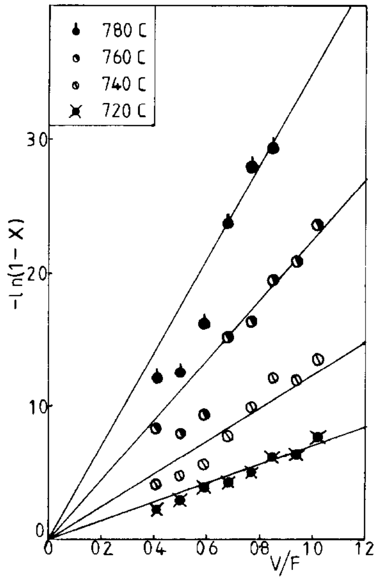


Fig 2 First-order plots of heptane pyrolysis

Whereas the activation energy derived in the present work compared reasonably with that reported by Bajus et al. [18], it was significantly lower than that obtained by Appleby et al. [27]. The good agreement shown by the *E* values derived in this work and by Bajus et al [18] is not unexpected as stainless steel reactors were employed in both studies The higher *E* value

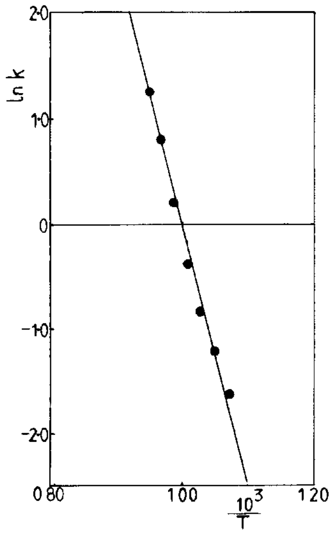


Fig 3 Arrhenius plot of the pyrolysis of heptane

TABLE 2

Comparison of kinetic rate parameters of n-heptane pyrolysis

	This work	Bajus et al [18]	Appleby et al [27]	Pease and Morton [25]
Temp range (°C)	660–780	680–760	550–630	530–560
Activation energy (kJ mol^{-1})	206 1	195 5	268 0	194 6
Pre-exponential factor (s^{-1})	$5\ 88 \times 10^{10}$	$1\ 34 \times 10^{11}$	–[a]	$7\ 08 \times 10^{9}$
Reactor material	Stainless steel	Stainless steel	Brass	Pyrex tube

[a] Not given

reported by Appleby et al [27] using a brass reactor may be due to the lower surface effects of brass compared to stainless steel The activation energy reported by Pease and Morton [25] is unexpectedly low, the Pyrex tube reactor used by them has relatively low surface effects [28] Furthermore, the pre-exponential factor derived in this work is comparable with that reported by Bajus et al [18]

Product distributions

The thermal cracking of n-heptane at 660–780 °C resulted in the formation of hydrogen, methane, ethylene, propylene, 1,3-butadiene and 1-butene as the major products, the minor products included ethane, propane, 3-methylbutene, 1-pentene as well as 1-hexene and benzene The composition of the product mixture is evidence of the complexity of the pyrolysis reactions of n-heptane Furthermore, the presence of benzene in the product mixture confirms the occurrence of dehydrogenation and dehydrocyclization steps in the complex mechanism The plots of product selectivities versus conversion (Fig 4a–c) show that the primary products of n-heptane pyrolysis were ethylene, propylene, methane, 1,3-butadiene and the higher α-olefins (1-butene, 1-pentene and 1-hexene), benzene was a secondary product Selectivities of ethylene and methane increased with n-heptane conversion, while that of propylene passed through a broad maximum On the other hand, selectivities of 1-butene, 1-pentene and 1-hexene decreased from their maxima Thus, the higher α-olefins undergo secondary reactions leading eventually to the formation of mono- and polynuclear aromatics, methane, hydrogen, ethylene and propylene [19] This is supported by the presence of benzene as a secondary product, the monotonic increase of methane selectivity with conversion and the substantial quantities of hydrogen formed in this work

Furthermore, the total gas yield (weight per cent of feed) increased with n-heptane conversion (Fig 5) this plot showed a near linear relationship It

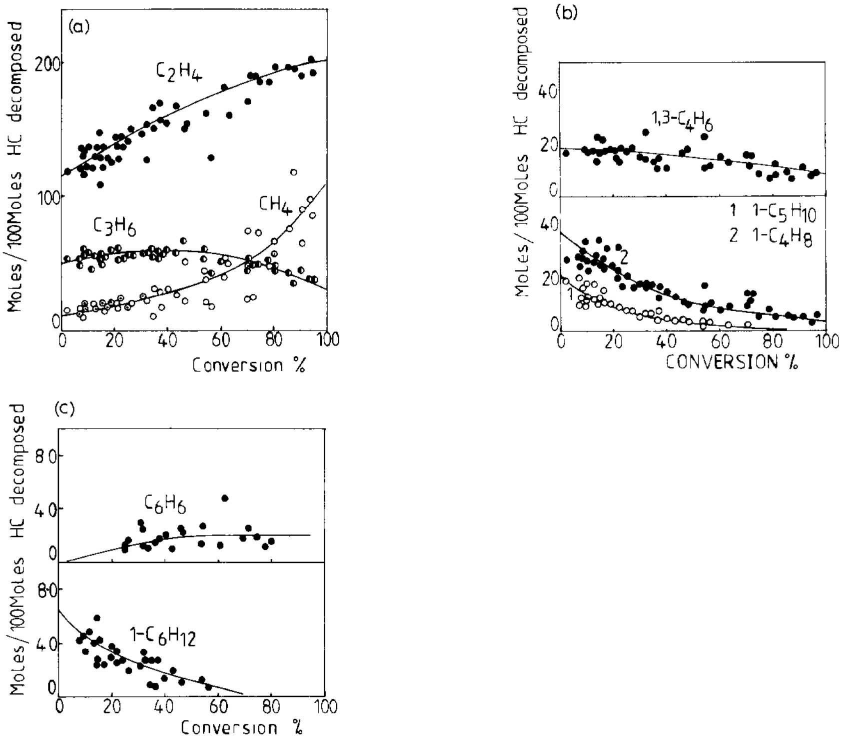


Fig 4 Product selectivities versus conversion in the pyrolysis of n-heptane

is characteristic of liquid hydrocarbon pyrolysis [16,18] It may be inferred from this plot that the total gas yield could be a good measure of conversion in the pyrolyses of liquid hydrocarbons The comparison of Fig 6 (product selectivities versus total gas yield) with Fig 4a clearly supports this conclusion

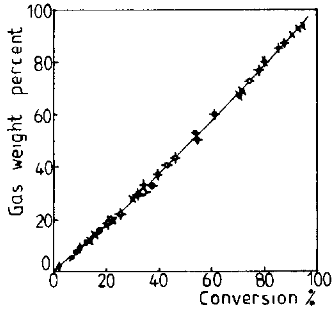


Fig 5 Gas production as a function of the conversion of heptane (○) 660 °C, (⊘) 680 °C, (✖) 700 °C, (⌖) 720 °C, (-○-) 740 °C, (⧫) 760 °C, (●) 780 °C

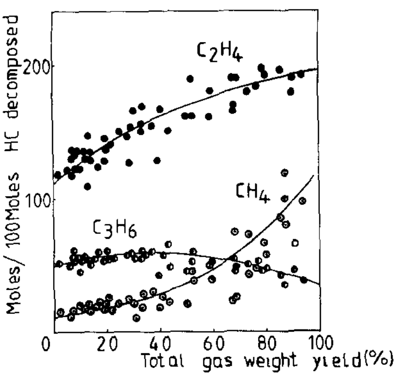


Fig 6 Product selectivities of n-heptane pyrolysis against total gas weight yield

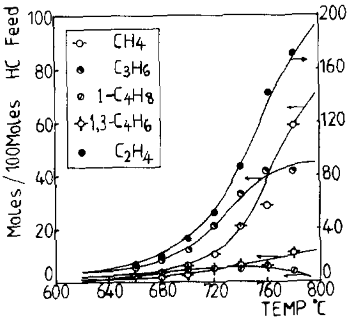


Fig 7 Product yields of the pyrolysis of heptane versus temperature, $\tau = 0\ 68$ s

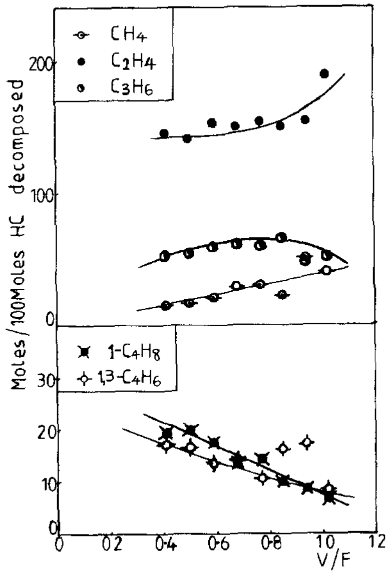


Fig 8 Product selectivities of the pyrolysis of heptane versus V/F at 720 °C

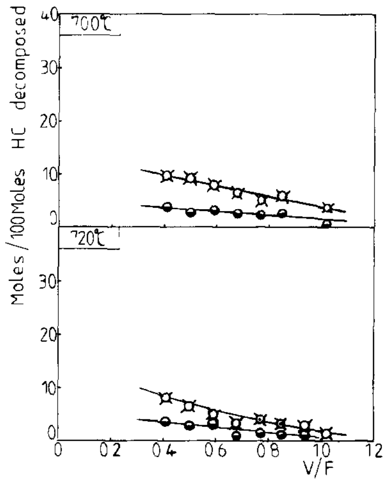
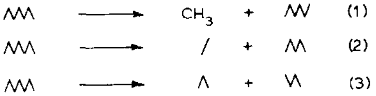


Fig 9 Product selectivities of the pyrolysis of heptane versus V/F (¤) 1-C_5H_{10}, (●) 1-C_6H_{12}

Figure 7 shows the typical variations of the product yields of n-heptane pyrolysis with cracking temperature Whereas yields of ethylene and methane increased monotonically with temperature, 1,3-butadiene yield increased slightly at all the residence times investigated Also, propylene yield tended to go through a maximum at temperatures greater than 760 °C, while 1-butene yield generally passed through a broad maximum Also, selectivities of ethylene and methane increased with residence time, while those of 1,3-butadiene, 1-butene, 1-pentene and 1-hexene decreased (Figs 8 and 9) On the other hand, propylene selectivity passed through a broad maximum with increasing residence time

Reaction mechanism

A reaction mechanism that accounts qualitatively for the product distributions of n-heptane pyrolysis is described below It is based partly on the free radical theory of Rice and Kossiakoff [14,15] The bond dissociation energy (BDE) of C–C bonds in C_2–C_8 hydrocarbons is 325–350 kJ mol^{-1}, whereas those for C–H bonds are 410–427, 393 and 381 kJ mol^{-1}, respectively, for the primary, secondary and tertiary positions [20] Consequently, under normal pyrolytic conditions primary initiation reactions of n-heptane pyrolysis are likely to be the unimolecular scission of primary and secondary C–C bonds



The experimental part of this work was conducted at high temperatures where the cleavage of C–H bonds to form heptyl radicals will also be

TABLE 3

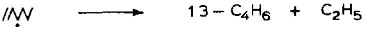
Comparison of experimental and predicted product distributions of n-heptane pyrolysis at 700 °C

Product selectivities (mol (100 ml decomposed n-heptane)$^{-1}$)	Experiment			Prediction
	This work	Bajus et al. [18]	Murata and Saito [21]	Rice–Kossiakoff theory ($E = 8.36$ kJ)
H_2	52.43	51.06	43	–
CH_4	17.43	49.52	47	53.84
C_2H_4	135.08	116.65	125	115.38
C_2H_6	3.37	6.18	17	46.15
C_3H_6	53.48	31.90	44	30.76
1-C_4H_8	24.16	21.30	27	15.38
1-C_5H_{10}	9.72	13.03	15	15.38
1-C_6H_{12}	3.96	6.00	7	15.38
	299.27	295.64	326	292.26

significant. Furthermore, smaller radicals (hydrogen, methyl, ethyl and 1-propyl) will undergo hydrogen abstractions with n-heptane molecules to form heptyl radicals. The higher alkyl radicals (butyl, pentyl, hexyl and heptyl) will undergo fast isomerization reactions followed by unimolecular decompositions to form ethylene, propylene and C_4–C_6 α-olefins and some smaller alkyl radicals. The substantially higher yield of ethylene is due not only to the unimolecular decomposition of ethyl radicals, but also to the β-scissions of the higher alkyl radicals.

To have further insight into the reaction mechanism of n-heptane pyrolysis, experimental product distributions were compared with those predicted using the R–K theory (Table 3), part of this table was adapted from the literature [18].

The selectivities of ethylene, propylene and 1-butene observed in this work were higher than those predicted by R–K theory, while methane, ethane, 1-pentene and 1-hexene were lower. The selectivities of some products observed by Bajus et al. [18] and Murata and Saito [21] were also not in good agreement with the R–K theory. Thus, the R–K theory is not completely sufficient in accounting for the product distributions of hydrocarbon pyrolysis. In explaining the low selectivity of 1-hexene observed in their work, Bajus et al. [18] suggested that it may decompose via an allylic radical to butadiene



(4)

They attributed the relatively low selectivities of ethane to the scavenging role of ethyl radicals and the catalytic activity of the reactor wall. They explained further that the ethane-forming step (reaction 5) is in direct competition with reaction 6 which is thermodynamically more favorable at normal pyrolytic conditions (high temperatures and low pressure)

$$C_2H_5 + RH \rightarrow C_2H_6 + R \qquad (5)$$

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (6)$$

However, this explanation is not comprehensive enough, it does not account for the lower selectivities of other higher alpha-olefins (1-butene and 1-pentene) and higher selectivities of ethylene and propylene relative to predictions by the R–K theory

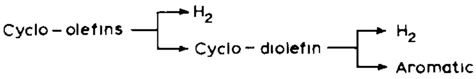
The disparities between the product distributions of n-heptane pyrolysis in this work and those predicted on the basis of the R–K theory may be rationalized in terms of the secondary decomposition reactions of the higher α-olefins Whereas the R–K theory predicts the formation of the higher α-olefins, it does not explain the secondary decompositions they undergo to form lighter products including hydrogen, methane, ethylene and propylene One set of these secondary reactions is the hydrogen-abstractions of the α-olefins (1-butene, 1-pentene and 1-hexene) with small radicals (most likely methyl and ethyl, and less likely hydrogen and allyl radicals [22]) Such hydrogen-abstractions form smaller parent radicals which may decompose to olefins or diolefins, they may also undergo dehydrocyclization reactions, to form cyclo-olefins

$$R' + C_NH_{2N} \xrightarrow{(a)} R'H + C_NH_{2N-1}$$

$$C_NH^{\bullet}_{2N-1} \xrightarrow{(b)} \left\{\begin{array}{l}\text{Olefins}\\ \text{Diolefins}\\ \text{Cyclo-olefins}\end{array}\right. + R'' \qquad (7)$$

where $R' = H$, CH_3, C_2H_5 and $C_3H^{\bullet}_5$, and $R'' = H^{\bullet}$, $C_2H^{\bullet}_5$, C_2H_3 and $C_3H^{\bullet}_5$

Under our experimental conditions, further dehydrogenation of the cyclo-olefins to form aromatics is important The presence of benzene as a secondary product in the present work supports this assertion (Fig 4c)



(8)

The second set of the secondary reactions of the α-olefins involves the addition of light free radicals (such as H and $CH^{\bullet}_3$) to α-olefins to form larger alkyl parent radicals, which, subsequently, decompose via β-scission to lighter olefins [22] Such reactions have been found to be significant in hydrocarbon pyrolysis reactions [23]

$$C_NH_{2N} + \left\{\begin{array}{l}H^{\bullet}\\ CH^{\bullet}_3\end{array}\right. \xrightarrow{(a)} \left\{\begin{array}{l}C_NH^{\bullet}_{2N+1}\\ C_{N+1}H^{\bullet}_{2N+3}\end{array}\right\} \xrightarrow{(b)} \left(\begin{array}{c}\text{Lighter}\\ \text{olefins}\\ +\\ \text{Radicals}\end{array}\right) \qquad (9)$$

Another significant pathway is the concerted molecular mechanism (retro-ene reaction) which splits the higher α-olefin C_NH_{2N} into C_3H_6 and $C_{N-3}H_{2N-6}$ [22], Thus, for one mole of 1-hexene two moles of propylene are formed However, the relative importance of the retro-ene reaction decreases with increasing temperature, and hence conversion This fact coupled with the secondary reactions of propylene account for the maximum exhibited by its selectivity with increasing conversion (Fig 4a) Furthermore, 1-butene decomposes at higher conversions to methane and ethylene [29] It is also significant to mention that concentrations of reactive light radicals (including $H^{\cdot}$, CH_3 and $C_2H_5^{\cdot}$) are relatively higher in paraffinic pyrolysis This assures that mechanisms proposed for the secondary decompositions of higher α-olefins are reasonably plausible Finally, the substantially high selectivities of ethylene and propylene may be attributed not only to the unimolecular decompositions of the alkyl radicals, but also to the secondary cracking reactions of 1-butene, 1-pentene and 1-hexene

CONCLUSIONS

It has been shown in this work that the R–K theory cannot adequately account for the formation of the products of n-heptane pyrolysis, particularly at high conversions The excesses and deficits of the products observed in this work compared with predictions by R–K theory have been rationalized in terms of the secondary decompositions of higher α-olefins Finally, the comparable product distributions and the good agreement between the kinetic rate parameters derived in this work and those in the literature confirm once more the adequacy of the pulse technique in studying the pyrolyses of hydrocarbons [16]

NOMENCLATURE

A	pre-exponential factor (s^{-1})
E	activation energy (kJ mol^{-1})
k	first-order rate constant (s^{-1})
T	temperature (°C or K)
X	conversion of n-heptane
τ	residence time (s)
V	reactor volume (ml)
F	volumetric flowrate of reactor effluent (ml s^{-1})
S	annular surface of reactor available for reaction (cm^2)

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