KINETICS OF THE THERMAL DECOMPOSITION OF CYCLOHEXANE

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ABSTRACT

The thermal decomposition of cyclohexane was studied in an annular flow reactor at atmospheric pressure and with nitrogen dilution. Experimental data were obtained in the temperature range 730—860°C and residence time range 0.161—0.482 s. The primary products were ethene, butadiene, propene and hydrogen. The overall kinetic analysis indicated the decomposition reaction to be approximately first order, with a frequency factor of 1.858×10^8 s^{-1} and an activation energy of 163.5 kJ mole^{-1}.

INTRODUCTION

The thermal decomposition of cycloalkanes in tubular reactors at temperatures above 600°C is of prime significance in petrochemical processes [1]. This is due to the current uncertainties concerning the availability of paraffinic pyrolysis feedstocks [2]. Paraffins give higher yields of desirable olefins [3,4]. This work was undertaken because most pyrolysis feedstocks (naphtha and gas oil) contain appreciable amounts of cycloalkanes [9,10].

The thermal decomposition of naphthenes produces not only ethene and propene but also some appreciable amounts of C_4 and C_5 dienes. There is scanty information in the literature on the thermal decomposition of pure naphthenes or their mixtures. Thus, the kinetics and mechanism of the pyrolysis of naphthenes have not been established. However, considerable research effort has been expended on the thermal decomposition of pure paraffins or their mixtures [3,8]. The pyrolysis of individual hydrocarbons or their mixtures with different properties is frequently studied for optimization purposes [1]. Cyclohexane is one of the cycloalkanes present in appreciable amounts in naphtha or gas oil. The results of this work should be useful in the design of commercial naphtha or gas oil cracking reactors.

The thermal cracking of alkanes at 600—900°C proceeds in the homogeneous phase according to a radical mechanism [1]. The formation of radicals is influenced by wall effects. Such surface effects can only be eliminated in a wall-less reactor [11]. The wall effects become more pronounced as the surface-to-volume ratio is increased; the qualitative and quantitative compositions of the product distribution are also affected by the reactor surface. Reactor surface affects reaction rates and the effect is known to be higher in iron than in quartz or gold reactors [12]. In addition, the tendency to form

coke is higher in iron, monel or cobalt than in quartz, porcelain, silver or gold reactors [13]. As regards the activation of the inner reactor surface, there is no agreement in the views expressed by workers in this area [1]. According to Crynes and Albright [14], the surface activation of walls by oxygen, hydrogen, steam or hydrogen sulphide influences the course of thermal decomposition. Kunzru et al. [15], however, did not observe this effect.

Coke deposition on the reactor wall is a serious problem which makes the study of the kinetics and mechanism of thermal cracking of hydrocarbons difficult. There is continuous change in the surface properties of the reactor as coke is mainly deposited on the reactor wall. This causes a continuous change in the composition of the product distribution. The reproducibility of the measurements, which requires constant reaction conditions, can be improved by decreasing the partial pressure of the compounds involved in the reaction by addition of an inert diluent [1]. Another possibility is the passivation of the inner reactor surface with surface-active agents.

In this paper, we report on the thermal decomposition of cyclohexane (a pure naphthene) using nitrogen as a diluent. Considerable attention was focused on the product distribution and the kinetics of the thermal decomposition of cyclohexane. The effect of surface on our kinetic studies is minimized by the use of nitrogen dilution.

EXPERIMENTAL

Materials

Cyclohexane (99.5% pure), supplied by the Hopkin and Williams Company, Essex, England, was used as the pyrolysis feedstock. The impurities contained in the feedstock are 0.011% cyclohexene, 0.01% benzene and 0.03% water. High-purity nitrogen purchased from Industrial Gases Ltd., Lagos, Nigeria, was used as a diluent without further purification.

Apparatus and procedure

The experimental set-up used in this investigation is similar to that previously reported by Susu and Ogunye [6], except a frigid flow bath circulator was used to provide cooling in the cold trap, instead of the ice chip—salt mixture used in ref. 6.

The pre-heater was set to give a temperature of about 600°C as all the experimental runs were performed at temperatures above 700°C. The frigid flow bath circulator was also set to a temperature range of 0—10°C so as to ensure sufficient cooling in the trap. The HPLC pump was maintained to deliver a particular amount of cyclohexane (about 21.36 g) into the system for all the runs. However, it was observed that the HPLC pump, at any particular setting, was not delivering the same amount of cyclohexane into the system. The diluent flow was found to influence the amount of cyclohexane delivered into the system. This diluent flow affects the hydrocarbon partial

pressure which in turn influences chemical equilibria and consequently the product distribution of the thermal decomposition of the hydrocarbon [16]. Maintaining a constant hydrocarbon partial pressure serves to eliminate any heat and mass transfer differences as well as the distortion of the relationship between conversion and residence time [17,18]. The feed partial pressure could be controlled by increasing the diluent flow rate or reducing the hydrocarbon feed rate [18]. In this investigation, however, the diluent flow rate once set was not altered. For all fixed diluent flow rates, the HPLC pump was adjusted to deliver the same amount of feed into the system for all runs.

The annular reactor outside-wall temperature was monitored every 2 min at a point mid-way along the reactor tube using Pt—PtRh thermocouples. The temperatures so measured were taken as the pyrolysis gas temperatures along the reactor tube. The reactor's axial temperature profile for each cracking temperature was also monitored by sliding a chromel—alumel thermocouple longitudinally in the inner-most tube of the annular reactor at intervals of 2 cm.

The gaseous effluent was passed through a condenser and the condensable components were condensed and collected in a cold trap. The non-condensables were passed through a sampling bottle into the atmosphere. The non-condensable effluent was collected in the sampler after 20 and 30 min of every run. Each experimental run was performed under steady state and a run was terminated before coke formation in the reactor caused significant deviation from the steady state. The onset of unsteady state behaviour was determined from noticeable variation in the chromatograms of the components of the gaseous effluent and/or flow rate of the effluent gas stream. Generally, steady state was attained within about 5 min and maintained for between 45 and 90 min, depending on the operating pressure and the nitrogen/hydrocarbon ratio.

Product analysis

The gaseous product samples were analysed using a Perkin Elmer Model 900 gas chromatograph in the manner reported previously [6]. In addition, the hydrogen content in the gaseous product samples was analysed with a thermal conductivity detector (TCD) using a Carbosiere E 45/60 mesh glass column under the following conditions: carrier gas = helium; column temperature = 100°C; manifold temperature = 250°C; injector temperature = 200°C.

The liquid product samples were analysed for cyclohexane and other liquid products including paraffins, olefins or cycle-olefins, using a 1.5 m × 2.33 mm internal diameter squalane column under the following conditions: carrier gas = nitrogen; column temperature = 160°C; manifold temperature = 250°C; injector temperature = 200°C.

Experimental runs were carried out in the temperature range 730—860°C and residence time range 0.161 and 0.482 s. The procedures used in the estimation of the weights of the various products analysed in the GC and the weights of coke produced in the reactor have been explained elsewhere [6].

RESULTS

In presenting the results of the thermal decomposition of cyclohexane, residence time (τ) was defined as

$$\text{Residence time (s)} = \frac{\text{(Effective volume of reactor)}}{\text{(Reactant flow rate at reaction conditions)}}$$

Product distribution

The product distribution of cyclohexane pyrolysis under any given reaction conditions depends on the temperature and conversion. The yields of the gaseous products increase with increasing conversion and the differences in the amounts of products at the same conversion level but different cracking temperatures are insignificant (Fig. 1). Molar selectivities (moles of product/100 moles cyclohexane decomposed) of the cyclohexane pyrolysis products (except hydrogen) obtained in the temperature range 730—860° C and residence time 0.161—0.482 s are shown in Table 1. The molar content of hydrogen in the gaseous products was only determined for runs at a residence time of 0.161 s.

The product distribution of cyclohexane decomposition consists of ethene, propene, 1,3-butadiene, methane and hydrogen. Small quantities of ethane, propane, and the butenes were also produced. The liquid product was predominantly cyclohexane (the reactant), with traces of benzene,
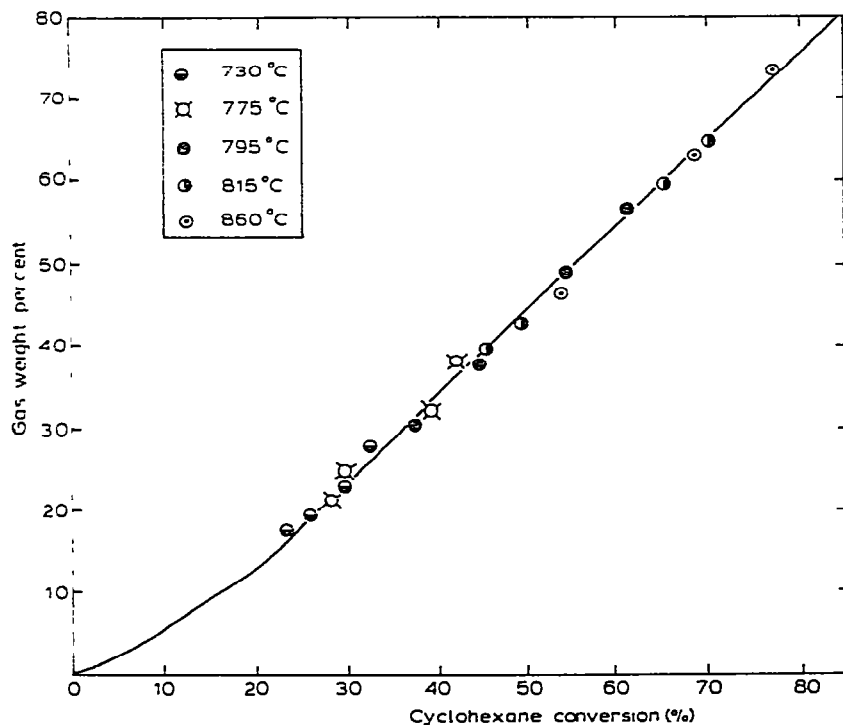

Fig. 1. Gas production as a function of cyclohexane conversion at different temperatures.

TABLE 1

Product distribution in pyrolysis mixtures of cyclohexane (moles/100 moles cyclohexane decomposed)

	τ = 0 161 s					τ = 0.241 s				
	730°C	775°C	795°C	815°C	860°C	730°C	775°C	795°C	815°C	860°C
Conversion (%)	23 5	28.6	37.5	45 6	49.2	26.2	29 9	44 9	49.7	54.0
Hydrogen	193.87	137 61	103.57	135.48	47 07					
Methane	11.40	18.39	19 57	17.86	13 69	3.46	6.69	12.92	7.50	10.95
Ethyne	1 90	3 77	0.93	1.42	5.85	0.40	1.14	1.24	0.70	2 40
Ethene	64 50	69 82	98.06	93.90	93.55	74.35	97.48	106 36	85.19	128.53
Ethane	15 97	1 79	2.33	2.29	6.09	2.88	3.77	4.15	3.33	5.11
Propene	17.02	20.04	5.22	18.23	17.67	12 09	15.52	19.16	12.52	13.27
Propane	0.78				3.29			3.79		
1,3-Butadiene	54.56	58.29	68.06	66.98	65.20	70.20	63.72	58.98	84.34	58.13
Butene	0.75	0.85	0.22	0.95	1.33		0.80	1.00		1.65

	τ = 0.321 s					τ = 0 482 s				
	730°C	775°C	795°C	815°C	860°C	730°C	775°C	795°C	815°C	860°C
Conversion (%)	29.8	39 3	54.4	65 6	69.1	32.7	42 2	61.4	70.1	77.2
Hydrogen										
Methane	8.65	5.47	9 58	12 44	8.47	6.42	2.59	12.13	12.83	20.39
Ethyne	2 78	0.89	8 35	2 25	7 03	1 35	0 88	0.50	1.41	2.95
Ethene	380.61	124 64	110.24	121 87	83.98	111.78	51 69	154.04	184.14	166.69
Ethane		0.84	0.76	0.82	0.55	7.12		9.20	12 71	4.18
Propene	26.58	16 87	17.71	18.34	12 02	30.31	27 41	29.68	18.09	16.42
Propane		0.42	0.26					0 10		
1,3-Butadiene	43 19	56.41	68.80	66.40	90 40	50 75	97.47	46.27	30.58	44.76
Butene				0 73				1.44		

cyclohexene and toluene; this is an indication that some dehydrogenation reactions are occurring to a slight extent. Figures 2 ansd 3 show the effect of cracking temperature on the molar selectivities of the product distribution of cyclohexane decomposition at a residence time of 0.161 s. Selectivities of ethene, butadiene, ethyne, ethane and butene-1 generally increased with increasing cracking temperature; those of propene and methane appear to be slightly independent of temperature.

Generally, coke was produced in small quantities except at the higher temperatures where appreciable amounts of it were deposited on the reactor inner surface. Coke yields (mass of coke/mass of initial cyclohexane) generally passed through a maximum at about 800°C for all the residence times investigated (Fig. 4). The coke yield curve for 0.241 s was found to be higher than that for 0.161 s, although the yield curves for 0.321 s and 0.482 s were observed to be lower than that for 0.161 s.

Figures 5 and 6 show the variations of the molar selectivities of ethene, 1,3-butadiene, propene, methane and ethyne with residence time at 795, 815 and 860°C. Ethene selecitivty tended to pass through a maximum and minimum with increasing residence time at higher pyrolysis temperatures; it
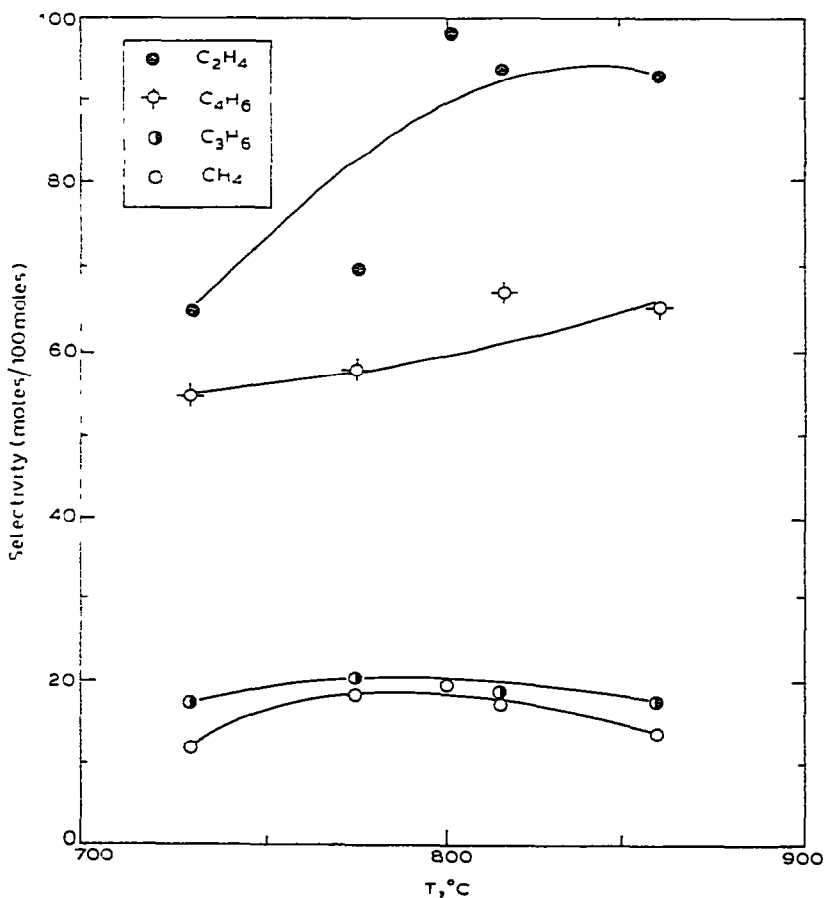

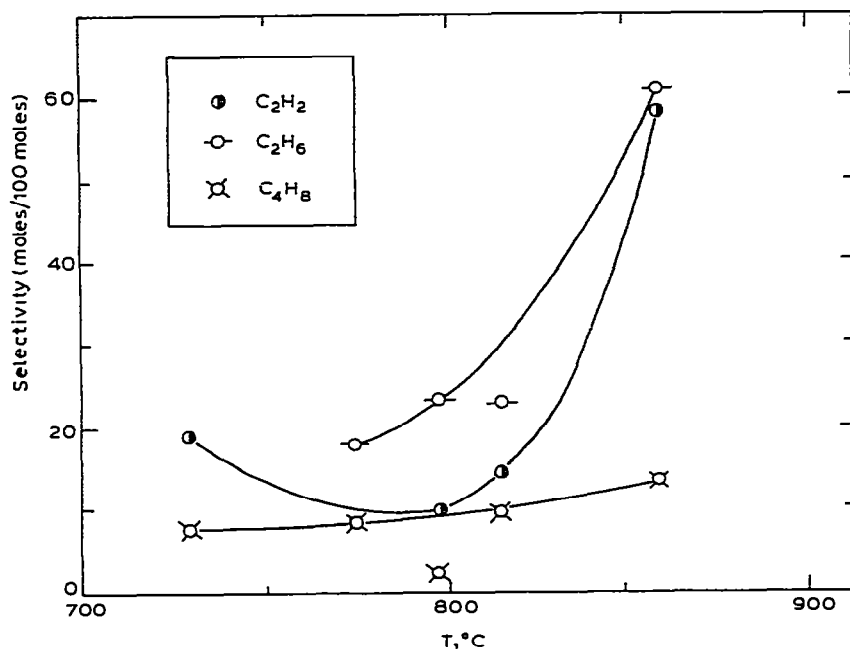Fig. 2. Molar selectivities of gaseous products vs. temperature for τ = 0.161 s.

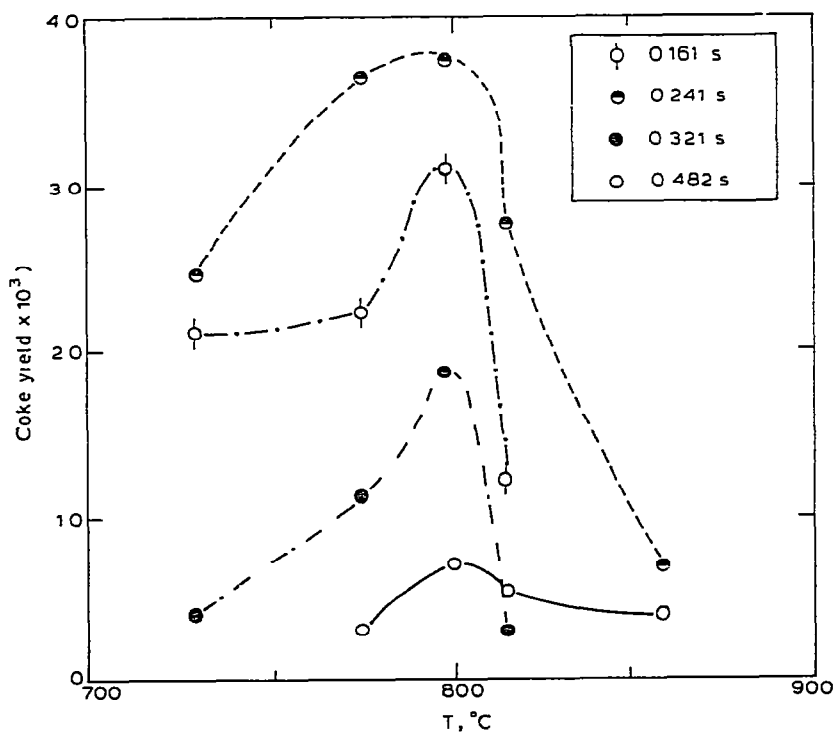Fig. 3. Molar selectivities of gaseous products vs. temperature for $\tau = 0.161$ s.

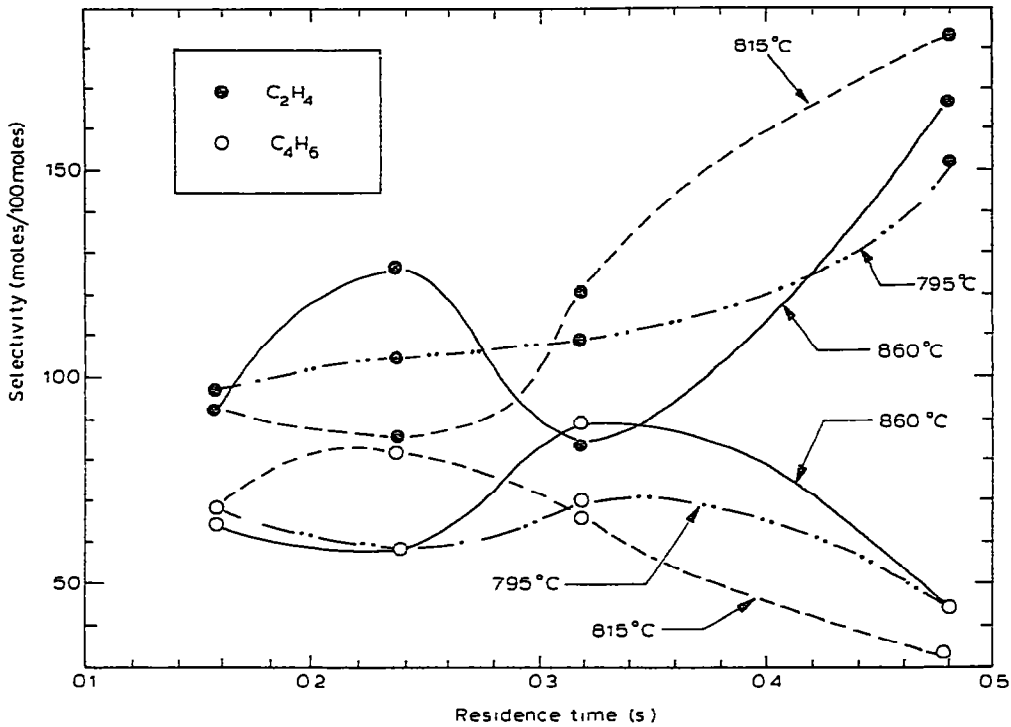Fig. 4. Coke yield vs. temperature.

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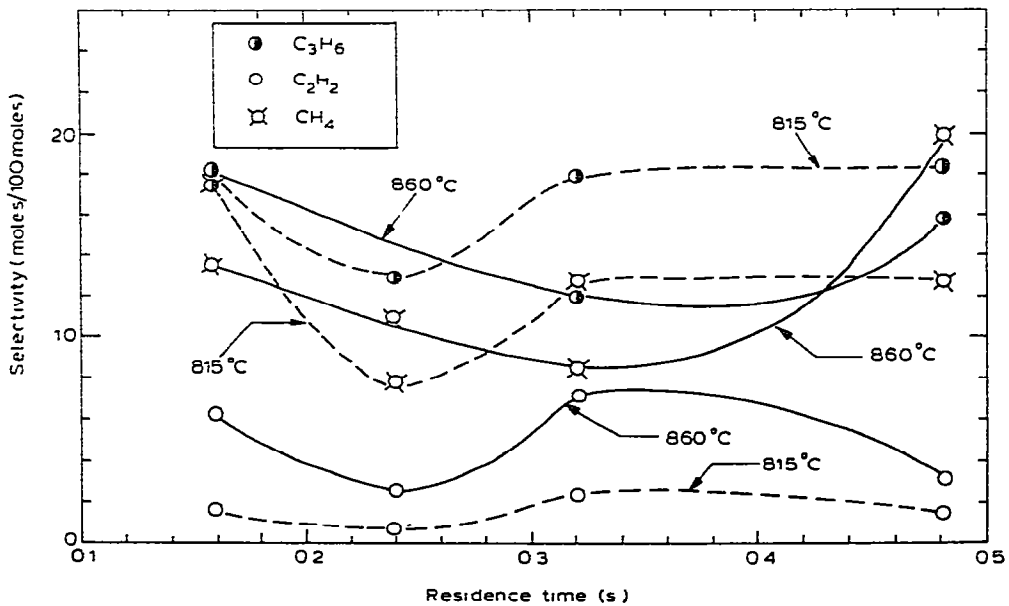Fig. 5. Molar selectivities vs. residence time of pyrolysis of cyclohexane.

Fig. 6. Molar selectivities vs. residence time of pyrolysis of cyclohexane.

increased with residence time at lower temperatures. However, 1,3-butadiene selectivity behaviour exhibited opposite trends.

Comparison of product distributions

A comparison of the product distribution obtained in this investigation with that of Levush et al. [19] is made in Table 2. This comparison was only made for the major products — ethene, butadiene, propene, methane and hydrogen. The comparison is not completely valid because this work was carried out under conditions different from those of Levush et al. [19]. It would, however, be useful in highlighting the differences in olefin yields during cyclohexane pyrolysis. The yields of light olefins (ethene, propene butadiene) obtained in the present work were surprisingly higher than those of Levush et al., in spite of the lower residence time and higher furnace temperature they used in their investigation. One suggestion for this discrepancy could be the type of reactor used in both studies. A highly roughened 304 stainless steel was used in this work whereas Levush et al. used a porcelain tubular reactor. The relative importance of surface-to-gas phase reactions increases in roughened metal reactors [22]; this roughening of surface also results in higher reaction rates and lower activation energies [22].

Kinetics of the thermal decomposition of cyclohexane

Cyclohexane was decomposed at temperatures between 730 and 860°C at atmospheric pressure using nitrogen as diluent. The frequency factor and the activation energy were determined by assuming that in a stationary reactor with plug flow the thermal decomposition of cyclohexane is an irreversible first-order reaction governed by the equation

$$\ln \frac{1}{1-x} = k\tau \tag{1}$$

where x = fractional conversion of cyclohexane, τ = contact time (residence time); and k = apparent overall reaction rate constant.

The conversion of cyclohexane to products depends on the temperature and residence time. The relation between the conversion of cyclohexane and the residence time for different temperatures is shown in Fig. 7. Figure 8 shows the plots of $\ln(1/1-x)$ against residence time (τ) at 730, 775, 795, 815, and 860°C. Table 3 contains the values of the rate constants determined from Fig. 8.

The rate constants derived from Fig. 8 do not decrease with increasing conversion because of the inhibition of the thermal decomposition by reaction products. The same is valid for the thermal decomposition of nonane in a stainless steel tubular reactor [16] and for the pyrolysis of heptane in a tubular stainless steel reactor using steam as diluent [1]. This observation confirms, as was the case for heptane, that the rate of the thermal decomposition of cyclohexane is governed by the first-order equation and is not affected by self-inhibition effects of some of the pyrolysis products. The absence of self-inhibition may be attributed to the presence of excess

TABLE 2

Comparison of product distribution of this work and that of Levush et al. [19]

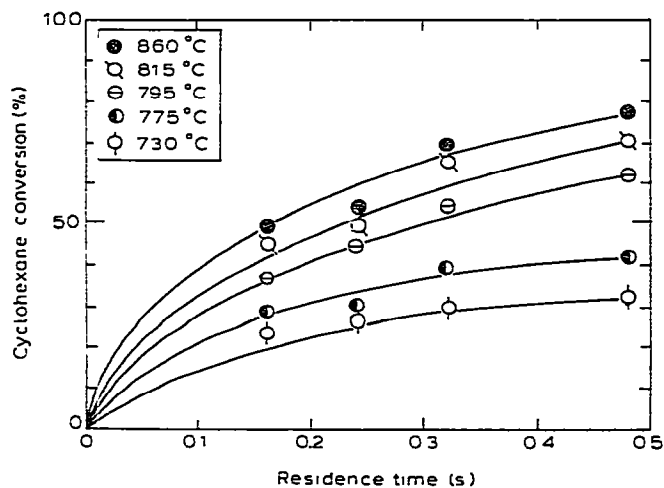|	Cyclohexane	
	This work	Levush et al.
Cracking conditions		
Diluent	Nitrogen	Nitrogen
Residence time (s)	0.161	0.001
Pressure	Atmospheric	Atmospheric
Temperature (°C)	860	900
Gaseous product yields (wt. fraction of feed)		
H_2	0.006	0.005
CH_4	0.013	0.008
C_2H_4	0.155	0.080
C_3H_6	0.043	0.021
C_4H_6	0.206	0.129
Reactor type	Stainless steel	Porcelain tube

Fig. 7. Conversion of cyclohexane as a function of residence time at different temperatures.

TABLE 3

Rate constants of the overall cyclohexane pyrolysis reaction

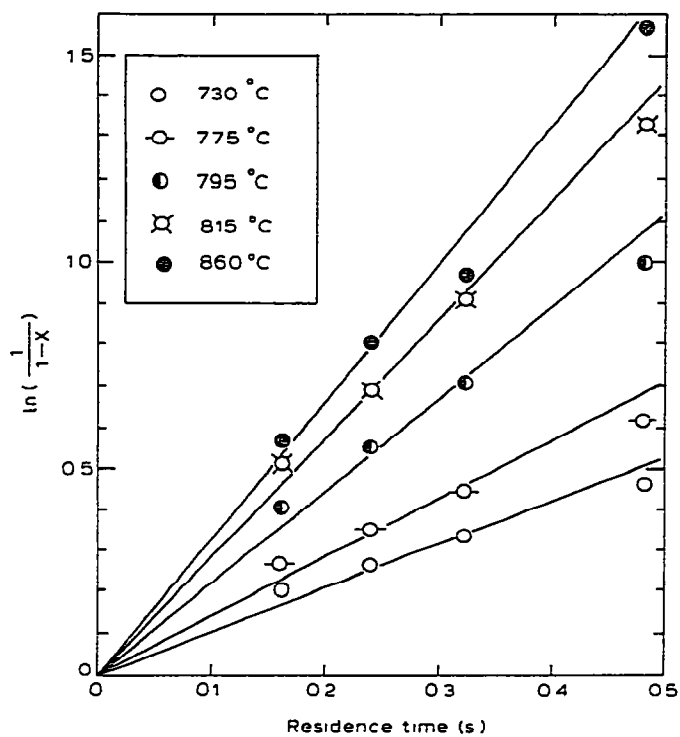| Temperature (°C)	Rate constant (s^{-1})
860	3.373
815	2.790
795	2.283
775	1.393
730	1.035

Fig. 8. Graphical representation of eqn. (1) for first-order reaction at different temperatures.
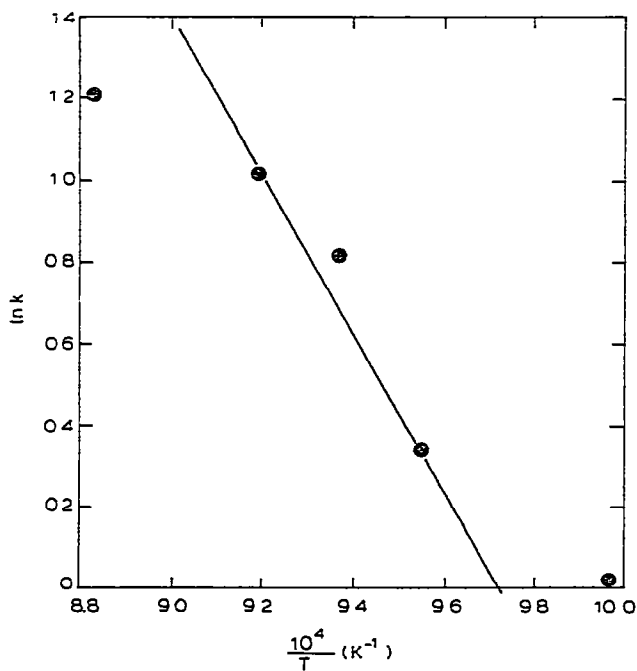

Fig. 9. Determination of activation energy for the pyrolysis of cyclohexane.

diluent. which reduces the partial pressure of reacting components [1]. This reduction in partial pressure in turn considerably reduces the progress of secondary reactions.

An Arrhenius plot for the cyclohexane pyrolysis is illustrated in Fig. 9. The rate parameters determined from the plot are: activation energy, E = 163.5 kJ mole^{-1}; and pre-exponential factor, A = 1.858 × 10^8 s^{-1}.

DISCUSSION OF RESULTS

The rate parameters obtained in the present work (E = 163.5 kJ mole^{-1} and A = 1.858 × 10^8 s^{-1}) are different from those obtained by other workers.

Levush et al. [19] found E = 288.9 kJ mole^{-1} and A = 3.24 × 10^{14} s^{-1}, whereas Kuchler [20] obtained E = 248.9 kJ mole^{-1}. The discrepancies in the values of the activation energies and pre-exponential factors are explained below.

The activation energy of 163.5 kJ mole^{-1} determined for the thermal decomposition of cyclohexane is substantially lower than the dissociation energy of a C—C bond (348.3 kJ mole^{-1}) [27] in a cyclohexane molecule. This behaviour was first reported by Bajus et al. [5]. They obtained a value of 201.3 kJ mole^{-1} as the activation energy for the thermal decomposition of methylcyclohexane. This was far lower than the C—C bond dissociation energy of 296.8—347.0 kJ mole^{-1} for a methylcyclohexane molecule. This observation, according to them, confirms the decisive influence of the heterogeneous mechanism at the surface of the reactor in the consecutive steps of the conversion of radicals originating from the initial hydrocarbons. By comparison, however, the homogeneous thermal decomposition of neo-pentane in a wall-less reactor occurs with an activation energy of 336.5 kJ mole^{-1}, which is in good agreement with the bond dissociation energy in neopentane [11]. The effect of the reactor inner surface on the homogenous mechanism depends on its area and quality (type of metal) [23]. The activation energy of the thermal decomposition of heptane is 242.4 kJ mole^{-1} in stainless steel, 223.6 kJ mole^{-1} in nickel and 138.8 kJ mole^{-1} in titanium reactors [21]. Roughening of metal reactors, due to usage, would result in higher reaction rates and lower activation energies [22]. The wall effect, therefore, influences both the kinetic factors of the conversion as well as the product distribution and yields of products. It would be reasonable to attribute the disparity in the activation energies obtained by the author, Levush et al. and Kuchler to the material of construction of reactor, activity of reactor surface and age (extent of usage).

The same reason can be invoked for the explanation of the low pre-exponential factor obtained in this work. The pre-exponential factor (A = 1.858 × 10^8 s^{-1}) is strikingly low compared to that reported by Levush et al. (3.24 × 10^{14} s^{-1}). It is even abnormally low when compared to the range of pre-exponential factors proposed by Benson [24] for first-order unimolecular fission reactions; the proposed range is 3 × 10^9—10^{16} s^{-1}, with most of them very close to the value of 10^{13} s^{-1}. As regards the few values that lie below this range, most seem explicable in terms of a reasonable decrease in

entropy accompanying the formation of a transition complex, whereas higher frequency factors reflect a reasonable entropy increase [24]. A suspiciously low A-factor probably represents a complex quantity rather than a true rate constant [25]. This could be true for pyrolysis reactions of most hydrocarbons; such reactions are generally believed to be complex due to the presence of secondary reactions in the reaction network. Reactions with abnormally small A-factors (such as 10^5 s^{-1} or smaller) are either heterogeneous or possibly chain reactions [24]. It is generally believed that pyrolysis reactions occur through free radical mechanism which involves chain processes (initiation, propagation and termination steps) [26]. Thus, the low pre-exponential factor can be attributed to the roughened reactor surface which affects the kinetic parameters in an as yet undetermined fashion.

NOMENCLATURE

A = Frequency factor (Arrhenius plot), s^{-1}.
E = Activation energy, $kJ\ mole^{-1}$.
k = first-order rate constant, s^{-1}.
T = Temperature, $^\circ$C or K.
X = Conversion cyclohexane.

Greek letters

τ = Residence time, s^{-1}

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