

## PYROLYSIS OF METHYLCYCLOHEXANE

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The kinetics of pyrolysis of methylcyclohexane was investigated from the viewpoint of coke formation in a steel tubular reactor ( $S/V = 6.65 \text{ cm}^{-1}$ ) at 0.1 MPa, 700 to 820°C and residence time 0.01 to 0.24 s. Decomposition of methylcyclohexane proceeds as a first order reaction with a frequency factor  $6.31 \cdot 10^{15} \text{ s}^{-1}$  and activation energy  $251.2 \text{ kJ mol}^{-1}$ . The course of secondary reactions associated with the formation of coke is discussed. Investigation of coke formation showed a greater tendency of methylcyclohexane to coking in comparison with heptane. A prominent role plays the course of dehydrogenation of cycloalkane radicals up to aromates, this being reflected by the overall conversion of methylcyclohexane, and, on the other hand the thus formed aromates enter the consecutive reactions leading to coke.

Cycloalkanes together with alkanes are well represented in all oil fractions able to be the feedstocks for pyrolysis. Their thermal cleavage afforded, in addition to ethylene and propene, also butadiene, isoprene and  $C_4$  and  $C_5$  alkenes in greater amounts; these are a demanded material in petrochemistry. Mechanism of thermal decomposition of cycloalkanes was reported in some papers; the majority of authors deal with the pyrolysis of cyclohexane as an individual compound<sup>1-8</sup>, or in a mixture with n-alkanes<sup>8-13</sup>. The mechanism of decomposition of cyclopentanes<sup>14</sup>, cyclohexanes<sup>15,16,18</sup>, higher cycloalkanes<sup>17</sup> was examined by Bajus *et al.* The effect of the side-chain length in the homologous series of alkylcyclohexanes on the value of kinetic parameters was described in<sup>19,20</sup>. The mechanism of decomposition of cycloalkanes with respect to the number of carbons in the ring (cyclohexane to cyclododecane) was reported in<sup>19</sup>. Kinetic regularities governing the pyrolysis of methylcyclohexane and the effect of co-pyrolysis with n-alkanes were studied in<sup>21,22</sup>.

Coking is taking place on pyrolysis of cycloalkanes similarly as with other hydrocarbons. As generally known, alkanes are least susceptible to coke and the presence of aromates significantly promotes the formation of coke. Position of cycloalkanes in this process is least clarified. Also rare are papers concerning a complex investigation of coke formation during pyrolysis of cycloalkanes. Murphy and Carroll<sup>23</sup> dealt with kinetic parameters of coke formation during pyrolysis of cyclohexane, cyclohexene and cyclopropane on a platinum surface in the 790 to 1100°C tempera-

ture range; an increase of activation energy in the sequence hexane < cyclohexane < cyclohexene < cyclopropane was observed.

This paper is aimed to examine the pyrolysis of methylcyclohexane under severe conditions, *i.e.* decomposition in the absence of an inert diluent. The main attention has been paid to the formation of coke, and, of course, to the kinetics and selectivity of thermal decomposition of methylcyclohexane. This contribution is a continuation of results obtained on pyrolysis of methylcyclohexane in the presence of steam<sup>16</sup>, where the conversions were lower (from 5 to 50%). This study was directed towards investigation of kinetics of thermal decomposition of methylcyclohexane.

Comparable reaction conditions with those proposed for pyrolysis of heptane were applied<sup>24</sup> with the goal to proceed decomposition under conditions considerably favouring secondary reactions leading to an enhanced formation of coke.

## EXPERIMENTAL

Methylcyclohexane was pyrolyzed both with the same flow equipment and conditions already described in detail<sup>24,25</sup>. Methylcyclohexane was pyrolyzed in a steel U-shaped tubular reactor with an enhanced inner surface to reactor volume ratio ( $S/V = 6.66 \text{ cm}^{-1}$ ). The reactor was made of stainless steel containing 17.5% Cr, 9.4% Ni, 0.7% Mn, and 0.15% C. Purity of the methylcyclohexane (Fluka, Switzerland) was 99.6%. Experiments were carried out in the 700 to 820°C interval at 0.1 MPa, the methylcyclohexane feed being 5 to 80 g h<sup>-1</sup>. Weight of the coke formed was estimated after 1 h from the beginning of the experiment, when stabilization took place. At the same time, formation of gaseous and liquid products was investigated and the products were gas-chromatographically analyzed. Flow of the pyrolysis gas was estimated by multiple readings on the bubble flow-meter.

## RESULTS

*Kinetics.* Thermal decomposition of methylcyclohexane was examined at 700, 730, 750, 800, and 820°C. Dependence of the methylcyclohexane conversion on the residence time at the above-mentioned temperatures is plotted in Fig. 1. The reaction order was determined according to Kershenbaum–Martin method<sup>33</sup>. Graphic interpretation of the equation for determination of the reaction order is shown in Fig. 2. The values vary within 0.27 and 1.08 (Table I) and decrease with the increasing temperature, what indicates possible changes in the mechanism of methylcyclohexane pyrolysis. At 700 to 750°C a cracking of methylcyclohexane in gaseous phase can be involved; this process is characterized by approximately first reaction order. An increase of the pyrolysis temperature to 800°C and more was accompanied with an increase of activity of the inner reaction surface. Cracking of methylcyclohexane does no more proceed in gaseous phase exclusively, but it is catalytically influenced by the inner reactor surface. An increase in the catalytical activity of the reactor wall due to the risen temperature is consequently manifested by a decrease of the reaction order to a value close to zero.

Pyrolysis either in a reactor made of catalytically inert material (quartz) or in the presence of steam was influenced minutely only or not at all. Therefore, no attention has been paid to determination of the reaction order and decomposition of cycloalkanes was assumed to be an irreversible first order reaction. In spite of the fact that the order of reaction does not reach values close to 1 with all experimental

TABLE I  
The reaction order values for decomposition of methylcyclohexane at various temperatures

Temperature °C	Reaction order, $n$	
	graph	lin. regress.
700	1.08	1.02
730	0.94	0.98
750	0.89	0.74
800	0.52	0.67
820	0.27	0.26

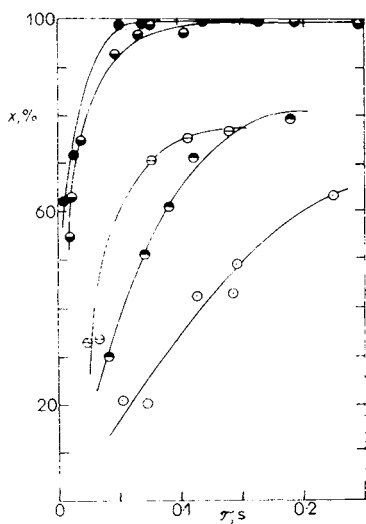


FIG. 1

Dependence of conversion on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at 700°C  $\square$ , 730°C  $\bullet$ , 750°C  $\circ$ , 800°C  $\bullet$ , 820°C  $\bullet$

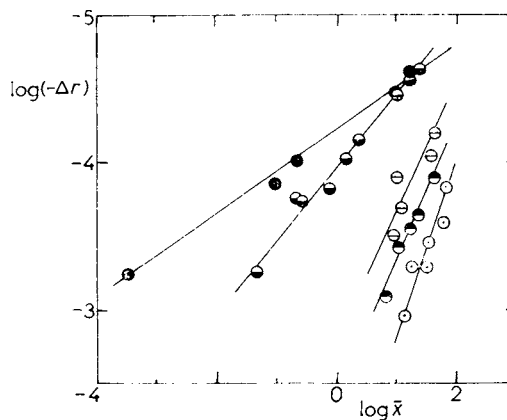


FIG. 2

Determination of the order of reaction for pyrolyses of methylcyclohexane at 700°C  $\square$ , 730°C  $\bullet$ , 750°C  $\circ$ , 800°C  $\bullet$ , 820°C  $\bullet$

temperature we neglect the catalytical influence of the reactor wall for simplification and we presume a first order reaction for this process. Equation (1) holding for irreversible first order reactions in a reactor with plug flow<sup>27</sup> was employed for calculation of the rate constant

$$k \cdot \varepsilon = (1 + \varepsilon) \ln \frac{1}{1 - x} - \varepsilon x. \quad (1)$$

Graphic adaptation of equation (1) showed an intersection of line dependences for various temperatures at zero conversion in one point corresponding to retention time 0.05 s. This phenomenon indicates an uncorrect estimation of the relative reactor volume, and consequently, also retention time values due to formation of a considerable amount of coke during pyrolysis of methylcyclohexane. Therefore, the relative reaction volume, determined according to the Hougen-Watson method<sup>28</sup> had to be corrected. Correction of the relative reactor volume represented the volume of the coke formed (2)

$$V_R = V'_R - V_K. \quad (2)$$

The graphic adaptation of equation (1) involving the corrected residence time is plotted in Fig. 3. The reaction rate constant values were determined by graphical,

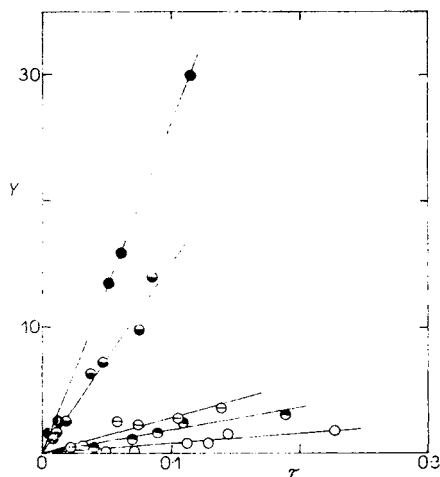


FIG. 3

Graphical adaptation of the Arrhenius equation for decomposition of methylcyclohexane at 700°C ○, 730°C ●, 750°C ⊙, 800°C ⊙, 820°C ●

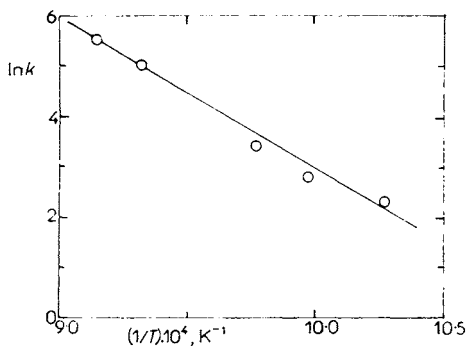


FIG. 4

Determination of activation energy for the pyrolysis of methylcyclohexane

linear regression and analytical methods (Table II). Differences between determinations of rate constants at predetermined temperatures estimated by the analytical method vary within 2 and 30%. No relationship between the rate constant values and conversion was found.

The kinetic parameter values determined by the Arrhenius equation according to calculated values of rate constants for the respective temperatures by the analytical method (Fig. 4) were found to be: activation energy  $251.2 \pm 7 \text{ kJ mol}^{-1}$  and the frequency factor  $6.31 \cdot 10^{15} \text{ s}^{-1}$ . Values of the known kinetic parameters for thermal decomposition of methylcyclohexane are listed in Table III just for comparison.

*Selectivity.* Alkanes and alkadienes are the main products formed by pyrolysis of methylcyclohexane, the other products being methane, ethane, hydrogen, and aromatic hydrocarbons. Amount of the gaseous products formed depends on the conditions of pyrolysis (Fig. 5). Extension of the residence time at 700 to 750°C

TABLE II

The rate constant values for conversion of methylcyclohexane at various temperatures

Temperature °C	$k, \text{ s}^{-1}$		
	graph	lin. regress.	analyt.
700	8	10.06	7.37
730	18	16.67	16.45
750	28	30.03	27.92
800	152	150.92	148.86
820	264	261.12	260.25

TABLE III

Kinetic parameters of pyrolysis of methylcyclohexane

Temperature °C	Frequency factor, $\text{s}^{-1}$	Activation energy $E$ $\text{kJ mol}^{-1}$	Ref.
720--830	$10^{12.55}$	242	29
	$10^{12.16}$	230	30
700--790	$10^{10.72}$	201	16
715--800	$10^{17.96}$	339	21
720--810	$1.2 \cdot 10^{16}$	317	20

favourizes formation of the gaseous products, and reaches its maximum at 800 and 820°C, this being accompanied with an increase of both the amount of coke and concentration of aromates in the liquid products. The error of experimental data concerning the amount of gaseous products varies from 5 to 15%. The average molecular mass of the gaseous products was estimated to be 18 to 27 g mol<sup>-1</sup>.

*The effect of temperature on formation of the profiling products.* Qualitative and quantitative comparison of the products of pyrolysis is presented in Table IV. The results were chosen so as the effect of temperature on yields of the respective hydrocarbons could be investigated at approximately the same residence times (0.05 and 0.11 s). Formation of ethane runs through a maximum; a similar course was found with propane at the residence time 0.05 s. Amount of the formed propane decreased with the increasing temperature, when extending the residence time to 0.11 s. Temperature has been found to influence the selectivity to ethylene, the amount of which rose from 26 to 85 mol *per* 100 mol of the methylcyclohexane reacted. Nevertheless, temperature differently influenced the formation of other alkanes: at 730°C propene and butadiene reached maximal yields.

The effect of temperature on formation of aromates is ambiguous. At soft conditions ( $\tau = 0.05$  s) the highest level of monoaromates (benzene, toluene) was attained at 750°C. At 0.11 s residence time, the temperature increase to 800°C was manifested by a decrease of benzene formation. The enhancement of temperature favoured formation of condensed aromates.

*Effect of retention time on formation of profiling products.* Investigation of the residence time on the formation of reaction products showed that only origination of methane has a univocal course. The level of methane slowly increases within the whole temperature range with the extension of residence time (Fig. 6). An ambiguous effect was seen with the formation of hydrogen (Fig. 7). Pyrolysis temperature 700 to 750°C and extension of the residence time sharply favoured its formation. Severe pyrolysis conditions (higher temperature, longer residence time) resulted in a slow increase of the yield of hydrogen, which passed through maximum. Examination of formation of profiling alkenes revealed a different behaviour at predetermined temperatures, ethylene being an exception. Increase of temperature up to 800°C and extension of residence time favoured its formation (Fig. 8). Formation of propene, 1,3-butadiene and isoprene was favoured by residence time only at 700°C. Severe conditions of pyrolysis (higher temperature and longer residence time) suppressed formation of the above-mentioned alkenes (Figs 9 to 11). Comparison of yields of alkenes from the pyrolysis of methylcyclohexane and heptane<sup>24</sup> disclosed that pyrolysis of the former afforded at low temperatures (700 to 730°C) almost the same amount of ethylene, but the yield of butadiene was by 10 times higher. Rise of the pyrolysis temperature resulted in lower yields of ethylene when compared with heptane and differences in formation of 1,3-butadiene were not so significant, even

TABLE IV  
Composition of the products of pyrolysis from decomposition of methylcyclohexane

Parameter	700°C	730°C	750°C	800°C	820°C
$V_R$ , ml	1.05	1.31	1.05	1.23	1.57
Residence time $\tau$ , s	0.05	0.11	0.11	0.11	0.12
Conversion $x$	21.01	42.68	30.06	76.24	99.9
Gaseous products, wt. %	6.84	24.4	26.6	50.74	56.0
Coke, wt. %	0.14	2.3	0.4	11.0	8.0

Product	mol/100 mol of methylcyclohexane decomposed									
Hydrogen	20.95	56.09	21.56	75.56	46.16	63.86	75.55	56.88	74.59	90.06
Methane	32.05	57.23	52.82	73.57	91.98	91.29	72.07	114.97	85.31	115.56
Ethane	6.91	11.96	6.59	12.77	12.68	15.65	12.64	11.68	9.17	7.13
Ethylene	26.09	41.33	66.51	62.66	62.66	49.10	56.61	75.45	85.01	88.64
Propane	0.76	1.96	1.99	1.16	2.30	1.30	0.61	0.56	0.56	0.26
Propene	14.68	26.41	40.33	30.68	29.21	28.50	17.83	18.36	15.32	7.82
1,3-Butadiene	7.82	13.33	31.76	18.77	9.56	13.37	12.91	3.95	10.64	4.31
Isoprene	0.70	0.95	0.87	1.65	0.89	1.24	1.18	0.47	0.70	0.12
Benzene	1.95	9.56	5.40	10.22	9.53	9.59	6.38	8.49	5.02	6.89
Toluene	2.41	7.12	3.62	8.01	14.92	11.92	7.17	4.12	5.64	3.92

though pyrolysis of methylcyclohexane produced butadiene in greater amounts.

Aromatic hydrocarbons are, in addition to the unreacted methylcyclohexane, the substantial portion of the pyrolysis products. The temperature increase favored

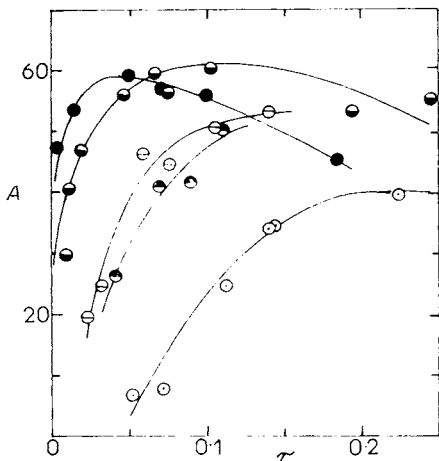


FIG. 5

Dependence of the gaseous products formation  $A$  (wt. %) on the residence time  $\tau$  (s) for pyrolyses of methylcyclohexane at 700°C  $\odot$ , 730°C  $\ominus$ , 750°C  $\oplus$ , 800°C  $\omin�$ , 820°C  $\bullet$ .

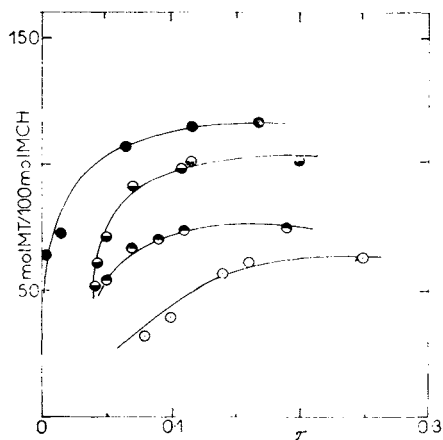


FIG. 6

Dependence of methane (ME) formation on the residence time  $\tau$  (s) for pyrolyses at 700°C  $\odot$ , 730°C  $\ominus$ , 800°C  $\omin�$ , 820°C  $\bullet$ .

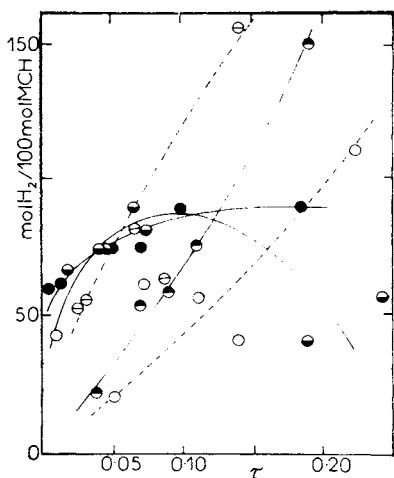


FIG. 7

Dependence of hydrogen formation on the residence time  $\tau$  (s) at 700°C  $\odot$ , 730°C  $\ominus$ , 750°C  $\oplus$ , 800°C  $\omin�$ , 820°C  $\bullet$ .



this formation, but the effect of residence time is ambiguous. The necessary residence time for formation of the maximal amount of benzene and toluene decreased with increasing temperature (Figs 12, 13). At 800°C and more, condensed aromates were formed; their yields mildly rose with an increased residence time.

*Coking.* Methylcyclohexane considerably tended to coke even at soft conditions. At 700°C, when pyrolysis is even more severe (longer residence time), the coke

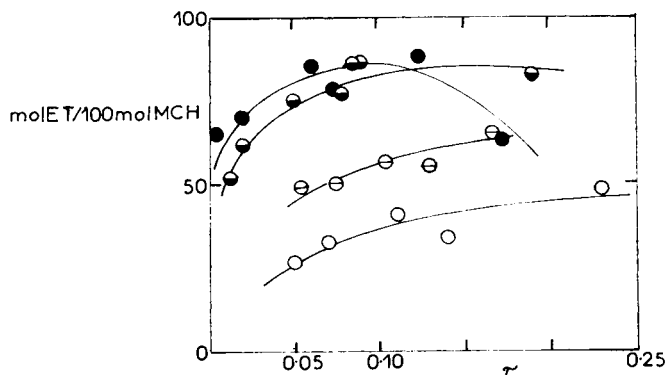


FIG. 8

Dependence of ethylene (ET) formation on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at 700°C ○, 750°C ◐, 800°C ◑, 820°C ●

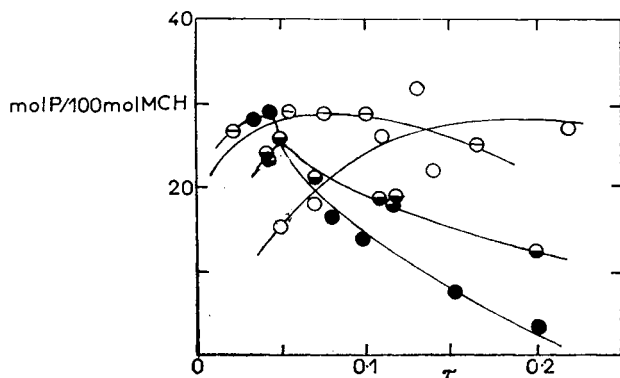


FIG. 9

Dependence of propene (P) formation on the residence time  $\tau$ (s) for pyrolyses at 700°C ○, 750°C ◐, 800°C ◑, 820°C ●

formation is higher. An increase above 750°C no more noticeably influenced coking (Fig. 14). The amount of coke linearly increased with changing the residence time.

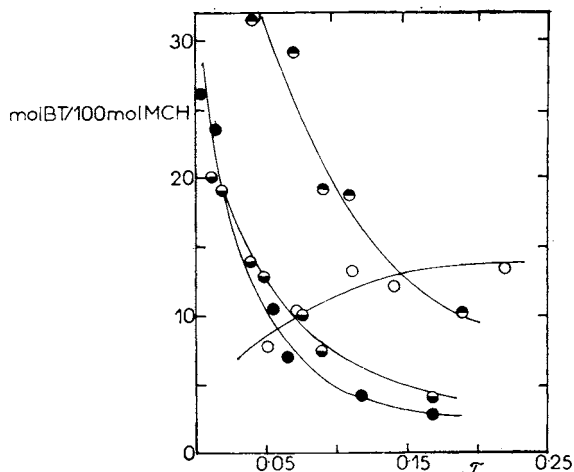


FIG. 10

Dependence of 1,3-butadiene (BI) formation on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at 700°C ○, 730°C ○·, 800°C ○—, 820°C ●

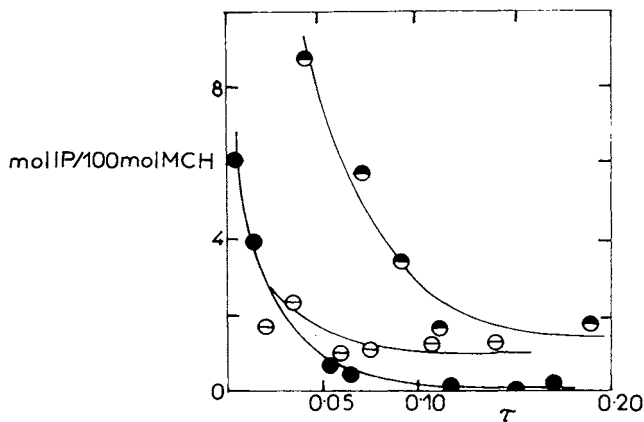


FIG. 11

Dependence of isoprene (IP) formation on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at 730°C ●, 750°C ○·, 820°C ○—

At stationary conditions, coking proceeded by a constant rate, what is characteristic of surface reactions having the zero order. In addition, also the course of coking during the experiment was examined (Table V); the amount of coke produced after 15, 30, 45, and 60 min was recorded. The production of coke reached its maximum within 15 min (*cf.* the maximal coking rate, Fig. 16).

## DISCUSSION

Pyrolysis of methylcyclohexane is accompanied with cleavage of C—C and C—H bonds to produce radicals (Scheme 1, reaction *a*). Comparison of dissociation

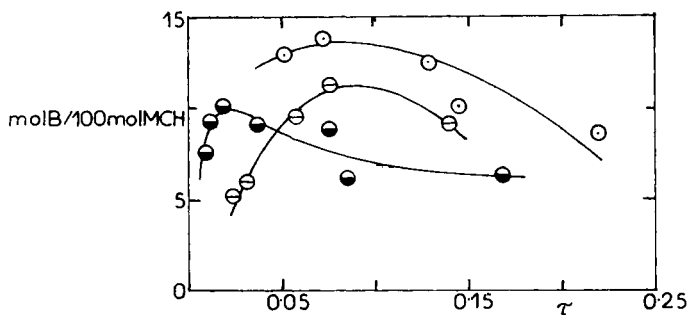


FIG. 12

Dependence of benzene (B) formation on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at 700°C ○, 750°C ◐, 800°C ●

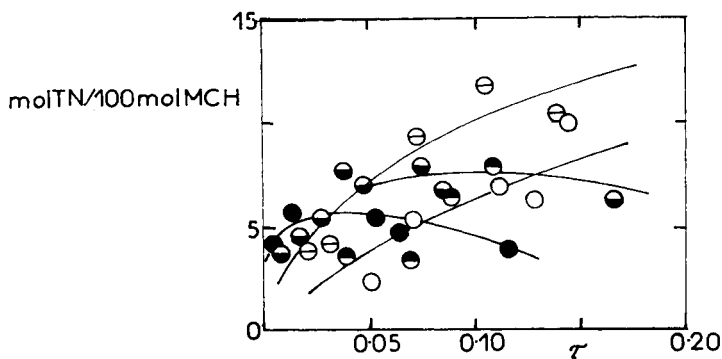


FIG. 13

Dependence of toluene (TN) formation on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at 700°C ○, 730°C ◐, 750°C ◑, 800°C ◒, 820°C ●

energies of the respective bonds disclosed the cleavage of bonds in cases *I* and *II* to be energetically least extensive. Values of dissociation energies vary about  $336 \text{ kJ} \cdot \text{mol}^{-1}$  (Table VI) and therefore, it could be presumed that in the initial phase of radical decomposition preferentially cycloalkane radicals originated; these give rise to alkanes (methane, ethane, propane), hydrogen (reaction  $b_1$ ) and alkenes (ethylene,

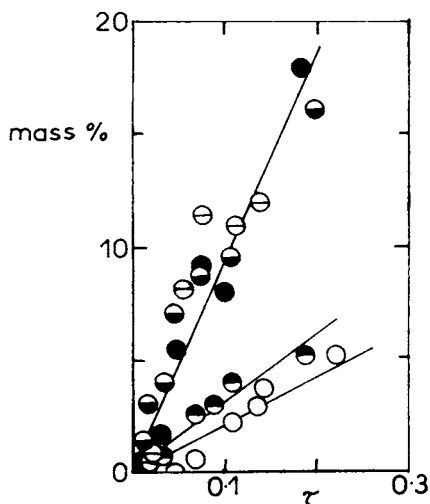


FIG. 14

Dependence of coke formation (wt. %) on the residence time  $\tau$ (s) for pyrolyses of methylcyclohexane at  $700^\circ\text{C}$   $\circ$ ,  $730^\circ\text{C}$   $\bullet$ ,  $750^\circ\text{C}$   $\ominus$ ,  $800^\circ\text{C}$   $\omin�$ ,  $820^\circ\text{C}$   $\bullet$

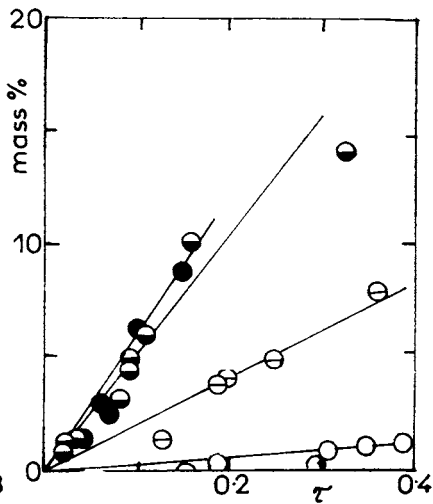


FIG. 15

Dependence of the coke formation (wt. %) on the residence time  $\tau$ (s) for pyrolyses of heptane at  $700^\circ\text{C}$   $\circ$ ,  $750^\circ\text{C}$   $\ominus$ ,  $800^\circ\text{C}$   $\omin�$ ,  $820^\circ\text{C}$   $\bullet$

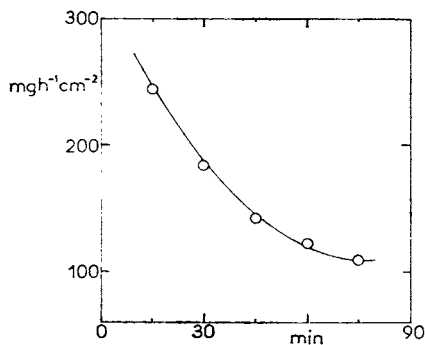
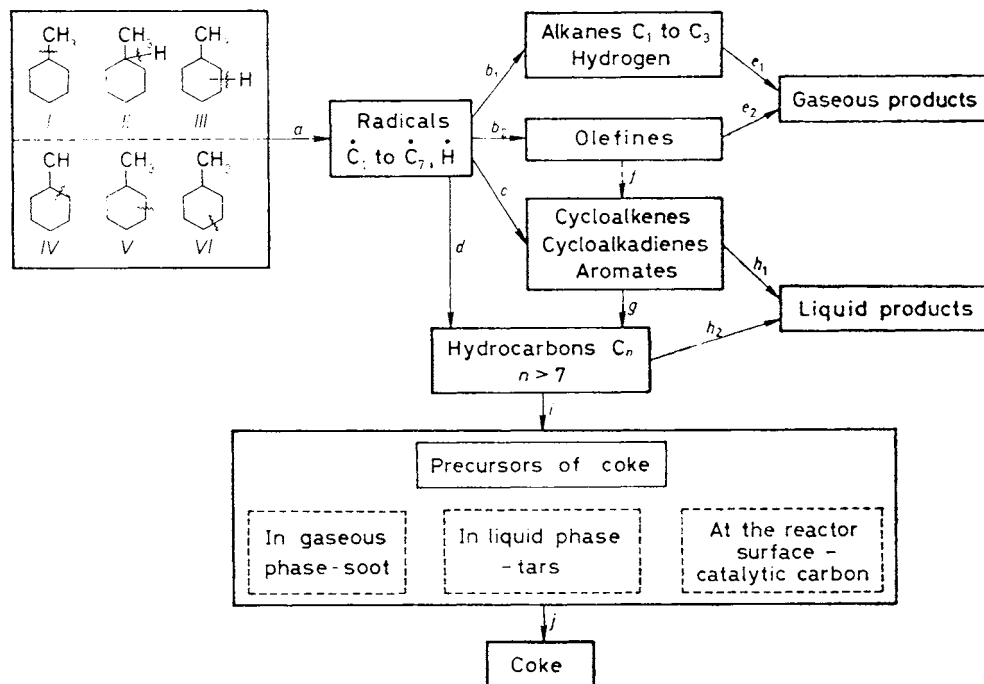


FIG. 16

Change in the coking rate with respect to duration of the experiment (min) for the pyrolysis of methylcyclohexane at  $800^\circ\text{C}$

propene, butenes, 1,3-butadiene, pentenes, isoprene (reaction  $b_2$ ) via a consecutive cleavage. These low-molecular alkanes and olefins form profiling components of the gaseous products ( $e_1, e_2$ ).



SCHEME 1

Even though in a substantially lower extent, cleavage of hydrogen from cycloalkane radicals takes place to afford cycloalkenes and aromates (reaction  $c$ ) concurrently with fission of methylcyclohexane to low-molecular alkanes and olefins

TABLE V

Effect of time,  $t$ , on the formation of coke during pyrolysis of methylcyclohexane (MCH)

Temperature, °C	800				820			
Residence time, s	0.08				0.09			
$t$ , min	15	30	45	60	15	30	45	60
MCH, g h <sup>-1</sup>	24.49	25.03	25.60	25.63	25.28	25.8	25.7	25.5
Coke, g	0.8	1.2	1.4	1.6	0.7	1.1	1.4	1.5

( $b_1, b_2$ ), this being in accordance with formation of benzene and toluene even at soft conditions (700 to 750°C). Benzene and toluene together with the unreacted methylcyclohexane are substantially represented in the liquid products ( $h_1$ ). Temperature rise favoured origination of polyaromates (reaction  $g$ ) – naphthalene, methyl-naphthalene, phenanthrene, and anthracene. At the same time, concentrations of benzene and toluene dropped. The course of dehydrogenation reactions was manifested by an enhancement of hydrogen content in gaseous products. So was the case especially at lower temperatures (700 to 750°C).

Cleavage of methylcyclohexane during thermal decomposition of hydrocarbons  $C_7$  proceeds in the presence of steam slower than that of heptane (Table VII, cf. refs<sup>16,26</sup>). This phenomenon is rationalized by a different mechanism of cleavage of the cycloalkane ring. If the cleavage of methylcyclohexane was due to opening of the ring (cases IV–VI), no propagation according to chain mechanism occurred, but bi-radicals were formed; these collapsed into molecular products. Pyrolysis of methyl-

TABLE VI

Values of dissociation energies for the respective bond types of methylcyclohexane (MCH)

Bond type in MCH	Dissociation energy <sup>31</sup> kJ mol <sup>-1</sup>
—CH <sub>2</sub> —CH <sub>2</sub> —	348.5
>CH—H	395—403
>CH—CH <sub>3</sub>	327—336
≥C—H	336

TABLE VII

Comparison of rate constants of pyrolysis of methylcyclohexane and heptane in the presence of steam

Temperature °C	$k, s^{-1}$	
	methylcyclohexane <sup>16</sup>	heptane <sup>26</sup>
700	1.19	2.28
740	2.98	7.64
750	4.70	14.41

cyclohexane in the absence of an inert diluent proceeded with almost the same activation energy as decomposition of heptane (Table VIII). The rate constant values for methylcyclohexane were mildly enhanced for the corresponding temperature. This finding let us presume that under these conditions just the concurrently proceeding dehydrogenation reactions increased the over-all rate of methylcyclohexane conversion in a decisive way. Providing the dehydrogenation ( $c$ ) and cleavage ( $b_1, b_2$ ) to products of decomposition proceed concurrently, and both are the first order reactions, then the rate constants of the individual reactions could be calculated and the additivity principle between the partial rate constants and the total rate constant must hold. The aromatic hydrocarbons and the adequate amount of hydrogen were considered when determining the concentration of hydrogenation products. The decomposition

TABLE VIII

Comparison of kinetic parameters of pyrolysis of methylcyclohexane and heptane in the absence of steam

Temperature °C	$k, s^{-1}$	
	methylcyclohexane	heptane
700	10.06	9.8
730	16.97	13.1
750	30.03	26.2
800	150.92	103.8
$E, kJ mol^{-1}$	251.7	255
$k_0, s^{-1}$	$2.54 \cdot 10^{14}$	$4.44 \cdot 10^{15}$

TABLE IX

Values of rate constants  $k$  of concurrent cracking and dehydrogenation reactions of methylcyclohexane at various temperatures

Temperature °C	$k, s^{-1}$	
	dehydrogenation	cracking
700	2.61	7.45
730	4.45	12.69
750	7.05	23.0
800	38.8	112.2
820	81.3	179.8

products were constituted by all remaining hydrocarbons and the rest of hydrogen. The values of rate constants for both parallel reactions indicated a faster course of decomposition with respect to dehydrogenation of methylcyclohexane (Table IX). The course of dehydrogenation was manifested by an increase of the total rate of conversion of methylcyclohexane by 23–26%. The presumption that dehydrogenation was catalyzed by the inner reactor surface could not be, however, excluded. In favour of this presumption is the finding that the change in the nature of the reaction surface (*e.g.* sulfidization) resulted in suppressing dehydrogenation and secondary reactions leading to formation of coke<sup>32</sup>.

Pyrolysis of hydrocarbons C<sub>7</sub> has also been considered as producing aromates from alkenes by secondary reactions of the Diels–Alder type (reaction *f*). These reactions, which are probably the one of the main ways to get aromates by pyrolysis of heptane<sup>24</sup>, require severe conditions (high temperature and long residence time). The hydrocarbon radical being present can further react with olefines and aromates by addition reactions to yield hydrocarbons of higher molecular mass (Scheme 1, reactions *d*, *g*). These hydrocarbons, having a polyaromatic character, can form coke precursors (reaction *i*), and in gaseous phase soot. Tars, forming fine drops in the reaction zone, condense on the cooler walls of the reactor and produce solid coating; catalytic carbon originated at the active centres of the reactor surface. All three components constitute coke (*j*).

Comparison of the ability to coking showed the substantially higher tendency of methylcyclohexane over heptane (Figs 14, 15), the most remarkable differences being found in the lower temperature range (700 to 750°C). The different coking behaviour of methylcyclohexane in contrast to heptane might be due to the mechanism of formation of cyclic or aromatic types. Concentration of aromatic hydrocarbons during the pyrolysis of methylcyclohexane is relatively high, even in the low temperature region, what is explained by a relative easiness of formation by dehydrogenation taking concurrently place with decomposition. On the other hand, pyrolysis of heptane has first of all to afford alkenes from which aromatic hydrocarbons originated by secondary reactions. This process requires, however, severe conditions. The increase of temperature is associated with formation of suitable conditions for production of aromates during pyrolysis of both feedstocks and differences in coking thus become unsubstantial.

It could be presumed that the principal portion of coke is being formed during pyrolysis on the inner surface of the reactor. Due to the metal surface, conversion of the high-molecular compounds of aromatic nature to catalytic carbon is taking place. A successive coating of the surface by the carbon layer results in the decrease of coking rate.



## LIST OF SYMBOLS

$x$	conversion
$k$	rate constant of the hydrocarbons decomposition, $s^{-1}$
$k_0$	frequency factor, $s^{-1}$
$E$	activation energy, $\text{kJ mol}^{-1}$
$R$	gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
$T$	experiment temperature, K
$V_R$	corrected equivalent reactor volume, ml
$V'_R$	uncorrected equivalent reactor volume, ml
$V_K$	equivalent coke volume, ml
$X$	average mole fraction of methylcyclohexane
$\Delta v$	rate of methylcyclohexane consumption, $\text{mol h}^{-1}$
$n$	order of the reaction
$\tau$	residence time, s
$\varepsilon$	relative volume change in the reaction

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