

important requirements include inhibitor availability, price, and boiling point. Adequate vapor phase protection and inhibitor distillation recovery is provided when the selected inhibitor and solvent boiling points are similar. The selected inhibitor must also not present any toxicity problems in the planned solvent use. The inhibitor must afford adequate inhibition at low concentrations (<5%) so that no high concentrations of flammable inhibitor vapors will concentrate in the chlorinated solvent vapor.

Selection of the final aluminum inhibitor may also be governed by other metals in the system since certain good aluminum inhibitors can cause corrosion problems with zinc and brass metals.

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Steam Cracking of Hydrocarbons. 2. Pyrolysis of Methylcyclohexane

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The thermal decomposition of methylcyclohexane in the presence of steam was studied in a laboratory tubular reactor with large inner surface at atmospheric pressure. Experimental data were obtained at a temperature range of 700–790 °C and at residence times of 0.04–0.20 s. The overall kinetic analysis gives a value of 201.3 kJ mol⁻¹ for the activation energy and $0.532 \times 10^{11} \text{ s}^{-1}$ for the frequency factor. The pyrolysis products (more than 90) were identified with capillary gas chromatography by comparison of their retention indices with those of standard hydrocarbons and by mass spectrometry.

Introduction

Our previous work (Bajus et al., 1979) dealt with the study of the pyrolysis of heptane in the presence of steam in a flow reactor with a large inner surface. In this work we present the results of a study of the thermal decomposition of methylcyclohexane under the same experimental conditions. This work was performed because the feed of industrial plants consists not only of alkanes but also of cycloalkanes and aromatic hydrocarbons. The presence of aromatic hydrocarbons is undesirable. Thermal decomposition of cycloalkanes yields not only ethene and propene, but also appreciable amounts of C₄ and C₅ dienes. The number of publications dealing with the pyrolysis of cycloalkanes is small as compared with alkanes. Attention has been focused mainly to cyclohexane. Reports on the pyrolysis of alkylcyclohexanes are scarcely found. The pyrolysis of methylcyclohexane, ethylcyclohexane, 1,1,3- and 1,3,5-trimethylcyclohexane (Bajus and Veselý, 1976a) has shown that these cyclohexanes produced higher yields of isoprene. The same is true for dimethylcyclohexanes (Mechtjev et al., 1959). The alkyl group exerts a considerable influence on the pyrolysis of alkylcyclohexanes. The composition of the reaction product mixture from the conversion of individual cyclohexanes is evidence for a complicated pyrolysis mechanism. We wish to report here on the mechanism and

kinetics of the thermal decomposition of methylcyclohexane. For elucidation of the thermal decomposition pathways of methylcyclohexane, detailed analysis of the pyrolysis products is necessary. Many diolefins are present in the liquid product mixture of the pyrolysis, and some of them are important intermediate products in the reaction.

Much work was devoted to the separation and identification of the reaction products by capillary gas chromatography and mass spectrometry.

Experimental Section

Materials and Methods. The experimental equipment used was the same as reported previously (Bajus et al., 1979). The thermal decomposition of methylcyclohexane proceeded in the presence of steam in a tubular reactor made from stainless steel with a large inner surface-to-volume ratio ($S/V = 6.65 \text{ cm}^{-1}$). The flow of methylcyclohexane was varied from 0.0634 to 0.361 mol h⁻¹ and that of water from 1.15 to 5.91 mol h⁻¹. The mass ratio of water to methylcyclohexane was 3:1 in all experiments. Distilled water was used. The methylcyclohexane was of 99.4 mass % purity (Fluka A.G., Chem. Fabrik, CH-9470 Buchs SG).

Analysis of gaseous and liquid products was made by the same procedure as in our previous work (Bajus et al., 1979). For obtaining the material balance we used capillary

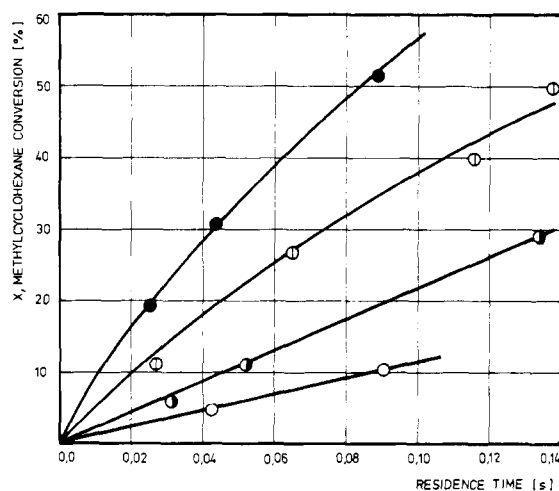


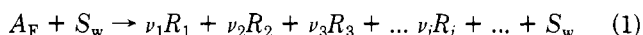
Figure 1. Conversion of methylcyclohexane as a function of residence time at different temperatures: ○, 700 °C; ●, 740 °C; ◐, 760 °C; ●, 790 °C.

columns coated with squalane and didecyl phthalate (length 50 m, i.d. 0.25 mm). For separation of methane, ethane, and ethene we used columns packed with florasil. Retention data of the compounds as well as the standard hydrocarbons were determined on a home-made chromatograph with a stainless steel capillary column (length 100 m, i.d. 0.25 mm). The same column was used in the combination GC-MS (Leferink and Leclercq, 1974).

Steam was selected as diluent purposely because of its wide usage in industrial pyrolysis units (plants). Steam converts the high boiling products and carbon to carbon oxides and secures constant conditions of pyrolysis which makes continuous cracking possible.

Kinetics of Thermal Decomposition

Methylcyclohexane was decomposed in the presence of steam at 700, 740, 760, 770, 780, and 790 °C at atmospheric overall pressure. The frequency factor and the activation energy were determined with the assumption that decomposition is an irreversible first-order reaction governed by the relations



and in a stationary reactor with plug flow

$$k \cdot \tau = (1 + \epsilon) \ln \frac{1}{1 - x} - \epsilon \cdot x \quad (2)$$

In eq 1 steam functions only as an inert diluent. For kinetic studies, the role of steam as reactant can be neglected (Bajus et al., 1979). The values of ν (moles of product formed per mole of methylcyclohexane decomposed) and ϵ (relative change of volume in the system when passing from zero to total conversion) were determined experimentally.

The conversion of the feed to reaction products depends on the temperature and the residence time. The relation between the conversion of methylcyclohexane and the residence time for different temperatures is shown in Figure 1. The right-hand term of eq 2 as a function of the residence time at the given temperatures is given in Figure 2.

The values of the rate constants determined from the graph in Figure 2 and the average values of the constants determined at given temperatures are summarized in Table I. The maximum standard deviation for numerically derived values is 23.4%.

The values of the rate constants do not show any decreasing trend as function of the conversion. The same

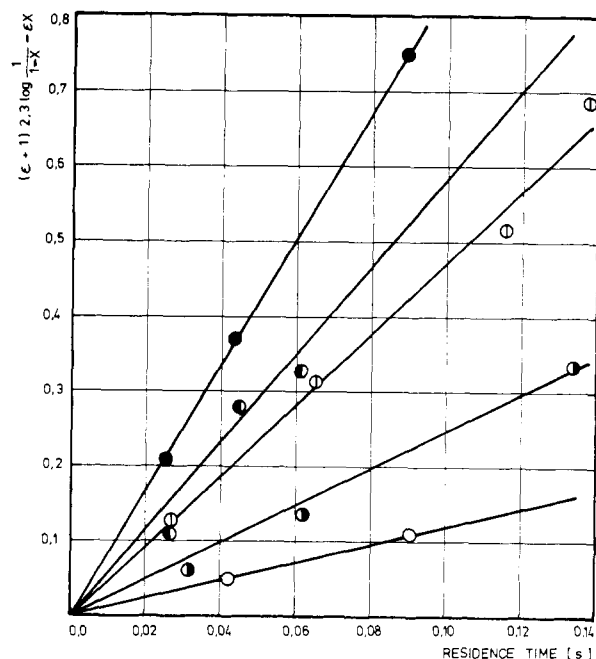


Figure 2. Graphic representation of eq 2 for first-order reaction at different temperatures: ○, 700 °C; ●, 740 °C; ◐, 760 °C; ●, 770 °C; ●, 790 °C.

Table I. Rate Constants of the Methylcyclohexane Decomposition

temp, °C	k_{anal} , s ⁻¹	std dev at anal. detn, %	k_{graph} , s ⁻¹
700	1.19	2.69	1.20
740	2.98	19.71	2.45
760	4.70	5.96	4.75
770	5.09	23.38	5.85
790	8.28	1.93	8.40

was true for heptane (Bajus et al., 1979) in identical experimental conditions. This confirms that the rate of the methylcyclohexane decomposition is governed by the first-order equation and is not influenced by self-inhibition effects of some pyrolysis products. The absence of self-inhibition may be correlated with the presence of a high excess of steam, which on one side lowers the partial pressure of reacting components and on the other side removes the high molecular components from the reaction system, thus minimizing the progress of secondary reactions.

The graphical adaptation of the Arrhenius equation for the determination of activation energy and frequency factor from the calculated rate constants is shown in Figure 3. The activation energy derived graphically is 201.3 kJ mol⁻¹ and the frequency factor 0.532×10^{11} s⁻¹. These values cannot be compared with any others as no data for methylcyclohexane have been published.

For the thermal decomposition of cyclohexane 248.9 kJ mol⁻¹ (Küchler, 1939) and 270.0 kJ mol⁻¹ (Illes et al., 1973) have been found. The activation energy for the decomposition of 4-methylcyclohexene to methane is 255.6 kJ mol⁻¹, to ethene 261.1 kJ mol⁻¹, and propene 271.5 kJ mol⁻¹ (Sakai et al., 1972). This comparison shows that the pyrolysis of methylcyclohexane in a tubular reactor of stainless steel in the presence of steam proceeds with the lowest activation energy. It is interesting to compare the kinetic parameters determined from the Arrhenius equation for heptane (Bajus et al., 1979) with those for methylcyclohexane. The value of the activation energy for the pyrolysis of heptane is 195.5 kJ mol⁻¹, which is practically, within the limits of the error, the same value

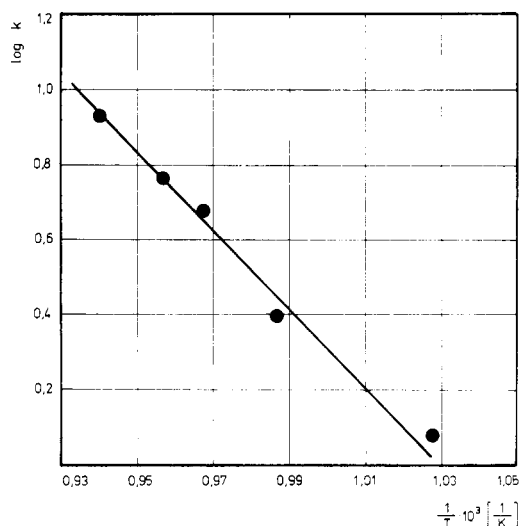


Figure 3. Determination of activation energy for the pyrolysis of methylcyclohexane.

as for methylcyclohexane. The frequency factor is $1.34 \times 10^{11} \text{ s}^{-1}$, again in good agreement. Under identical experimental conditions, therefore, the rate of decomposition of methylcyclohexane is 2.5 times slower than that of heptane.

Composition of the Product Mixture

Qualitative Analysis. Much attention was paid to the identification of products from the decomposition of methylcyclohexane at the given experimental conditions. This complicated mixture has not yet been analyzed in detail up to now.

Since many hydrocarbons are supposed to be present in the pyrolysis product mixture, a capillary squalane column was used to enhance the possibility for comparison with many precise data available in the literature (table matching).

Retention indices were measured with high precision at 50 and 70 °C at an inlet pressure of $2.5 \times 10^5 \text{ Pa}$. Nitrogen and hydrogen were used as carrier gas. Chromatograms of the reaction products are given in Figure 4 (nitrogen) for the lower boiling compounds and Figure 5 (hydrogen) for the higher boiling hydrocarbons. For the latter the analysis time could be reduced about 50% without loss in precision by using hydrogen instead of nitrogen as carrier gas at the same inlet pressure. Compared to nitrogen the retention indices with hydrogen will be systematically about 1.0 index unit (i.u.) lower for aromatics and somewhat less for cycloalkanes. For all other hydrocarbons this difference appeared to be within experimental errors ($<0.5 \text{ i.u.}$). No significant differences were registered between retention indices calculated from time measurements with a stopwatch or a digitizer-computer system with off-line data processing.

In total 93 peaks were identified, most of these by table matching with Kováts' retention indices published in the literature (Rijks and Cramers, 1974; Loewenguth and Tourres, 1968; Soják and Rijks, 1976; Hively and Hinton, 1968). The results are presented in Table II.

The hydrocarbons for which no retention data are given in the table were identified by direct comparison of retention times to those of standards. For about half of the hydrocarbons their identity was either confirmed or alternatives were excluded by mass spectrometry. The same column was directly coupled to the mass spectrometer. Some peaks (no. 30, 43, 64, 65, 81, 83) were identified only by mass spectrometry. In this case it is difficult to distinguish different isomers. Except in those experiments where retention indices were matched to data of Hively and Hinton (1968), the difference of measured and tabulated values was within experimental error ($<0.5 \text{ i.u.}$).

Quantitative Analysis. The composition of pyrolysis products at the given reaction conditions depends on the temperature and conversion. The yield of gaseous products increases with increasing conversion. At the same conversion level but at different temperatures the differences

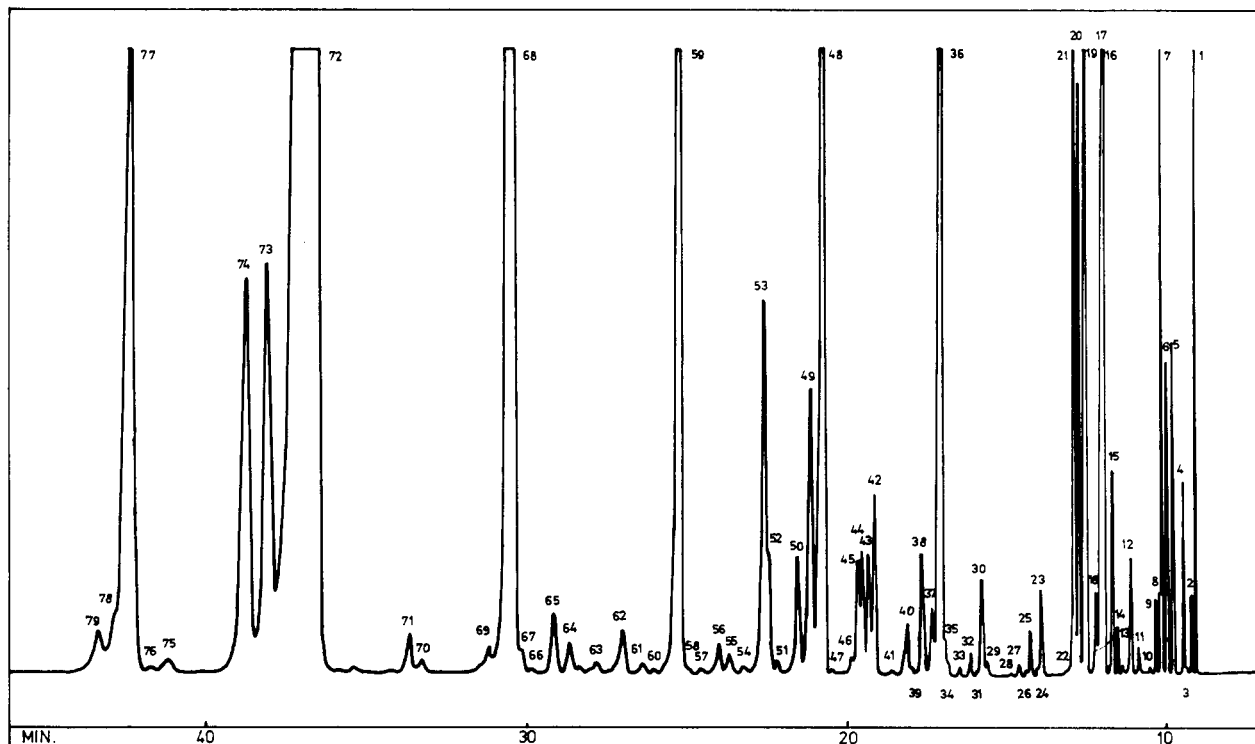


Figure 4. Chromatogram of products from pyrolysis of methylcyclohexane: temperature, 50 °C; carrier gas, nitrogen; inlet pressure, $2.5 \times 10^5 \text{ Pa}$.

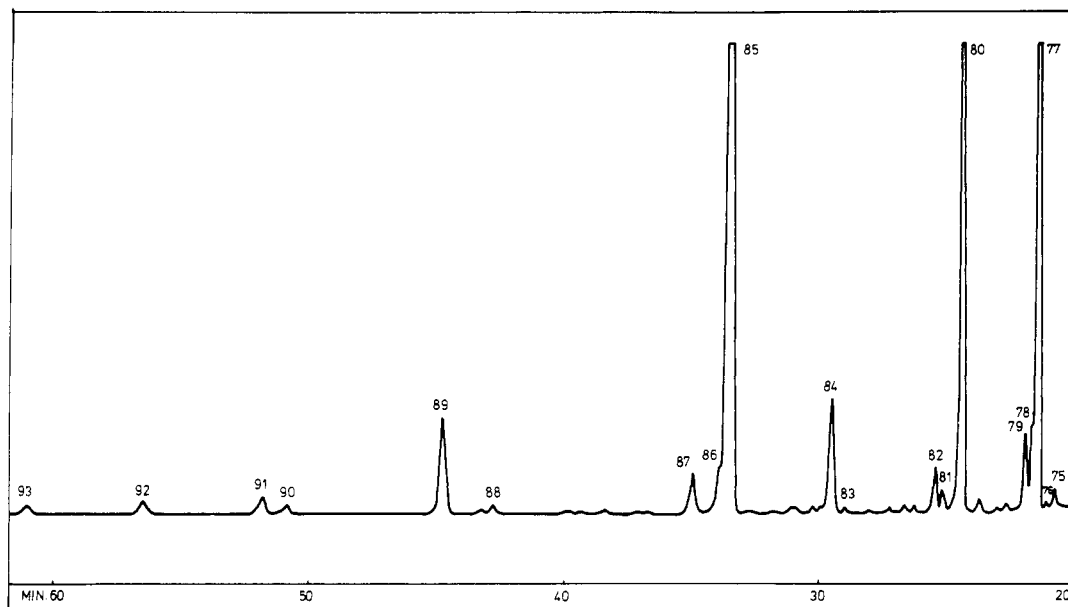


Figure 5. Chromatogram of products from pyrolysis of methylcyclohexane: temperature, 50 °C; carrier gas, hydrogen; inlet pressure, 2.5×10^5 Pa.

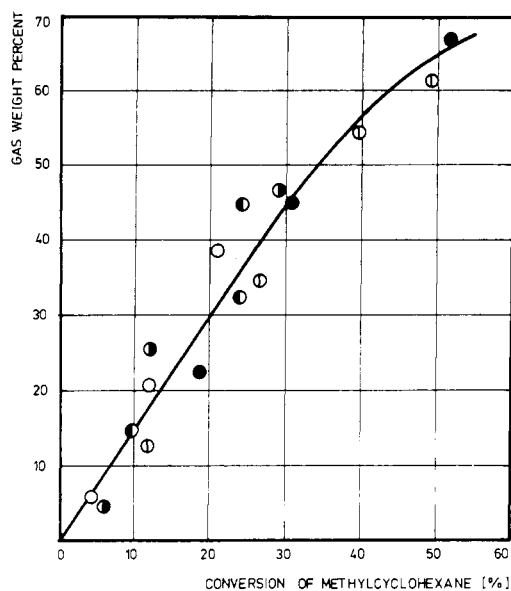


Figure 6. Gas production as a function of conversion of methylcyclohexane at different temperatures: ○, 700 °C; ◐, 740 °C; ◑, 760 °C; ◒, 770 °C; ●, 790 °C.

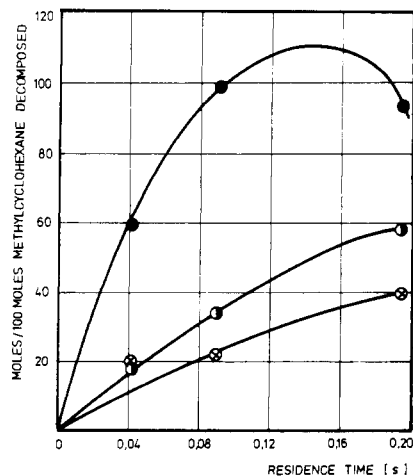


Figure 7. Product distribution vs. residence time of pyrolysis of methylcyclohexane at 700 °C: ●, ethene; ○, propene; ⊗, 1,3-butadiene.

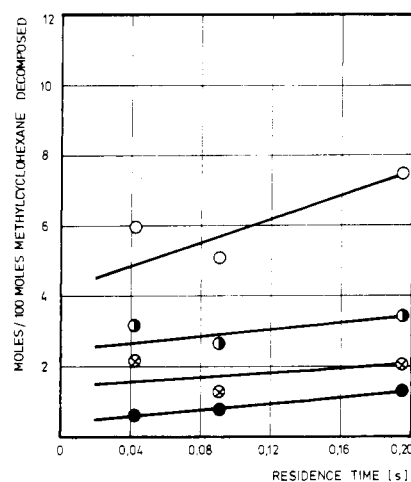


Figure 8. Product distribution vs. residence time of pyrolysis of methylcyclohexane at 700 °C: ○, isoprene; ●, 1,trans-3-pentadiene; ⊗, 1,cis-3-pentadiene; ●, 1,3-cyclopentadiene.

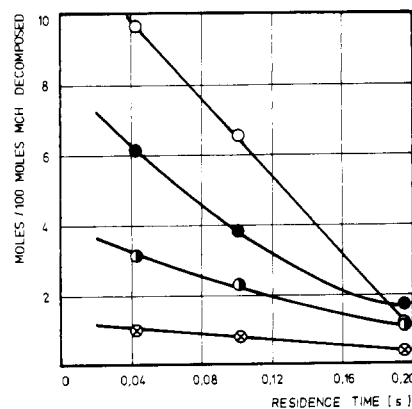


Figure 9. Product distribution vs. residence time of pyrolysis of methylcyclohexane at 700 °C: ●, 1-methylcyclohexene; ○, 4-methylcyclohexene; ⊗, 3-methylcyclohexene; ○, cyclohexene.

in the amounts of products are small (Figure 6).

The complete quantitative analysis of gaseous and liquid products is given in Table III with the exception of hydrogen and carbon monoxide. (For 100 mol of converted feed, 40 to 210 mol of hydrogen and 10 to 63 mol of carbon

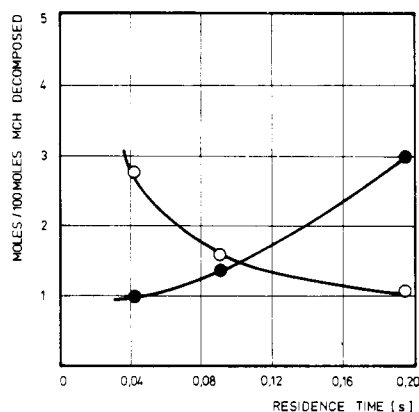


Figure 10. Product distribution vs. residence time of pyrolysis of methylcyclohexane at 700 °C: ●, benzene; ○, toluene.

monoxide are produced). The profiling products are ethene, propene, 1,3-butadiene, methane, isoprene, piperynes, cyclopentadiene, cyclohexene, and methylcyclohexenes. The influence of residence time on the selectivity of the pyrolysis of methylcyclohexane at 700 °C is shown in Figures 7 to 10. Figure 9 shows the unambiguous influence of residence time on the decrease of selectivity in the production of cycloolefins as important intermediates. The same trend has been found for the selectivity of the conversion of methylcyclohexane to toluene (Figure 10). Under the applied pyrolysis conditions, ethene, propene, 1,3-butadiene, and methane are the main products.

Discussion of Results

The activation energy of 201.3 kJ mol⁻¹ found for the decomposition of methylcyclohexane is substantially lower than the dissociation energy of -C-C- bonds (296.8 to 347 kJ). The thermal decomposition of methylcyclohexane proceeds in reaction conditions which are energetically on the same level as the pyrolysis of heptane (Bajus et al., 1979). This 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 hydrocarbon. By comparison, the homogeneous pyrolysis of neopentane, e.g., in a wall-less reactor proceeds with an activation energy of 336.5 kJ, which is in good agreement with the bond dissociation energy in neopentane (Taylor et al., 1969). The influence of the inner surface is not only proportional to its area, but also determined by its quality. The activation energy of the thermal decomposition of heptane has a value of 242.4 kJ mol⁻¹ in stainless steel, 223.6 kJ mol⁻¹ in nickel, and 138.8 kJ mol⁻¹ in titanium reactors (Melikadze et al., 1975). The wall effect influences not only these kinetic factors of the conversion, but also the composition of the reaction mixture and yields of products. The products of this reaction can be gaseous, solid, or both. In the conversion of methylcyclohexane no solid compounds are formed, because gasification at the wall is influenced by the presence of steam. Therefore the wall is free of carbon and high molecular products and deactivation does not occur. The low partial pressure of components in the system in an excess of diluent contributes to this effect. If the ratio of steam to methylcyclohexane is lowered, a fast change of the quality of the inner surface occurs as a consequence of coking.

The inner surface of a stainless steel reactor displays another characteristic property in the conversion of methylcyclohexane to low molecular alkanes. The yields of methane and ethane are lower than from a quartz reactor. Figures 11 and 12 show the ratio of methane and ethane

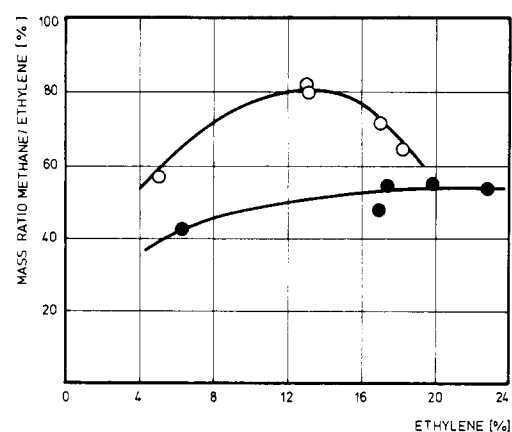


Figure 11. Ratio of methane to ethene vs. ethene concentration at 780 °C in stainless steel (●) and quartz (○) reactors.

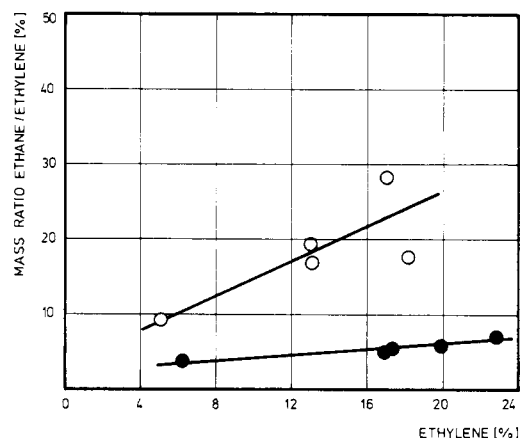
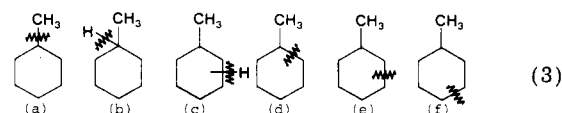


Figure 12. Ratio of ethane to ethene vs. ethene concentration at 780 °C in stainless steel (●) and quartz (○) reactors.

to ethene for both reactors at 780 °C in identical conditions. This property of the reaction system is not specific for methylcyclohexane, but is valid for other hydrocarbons too, e.g., heptane (Bajus et al., 1979), straight-run naphtha, and naphthas from catalytic reforming after the extraction of aromatic hydrocarbons (Bajus et al., 1977).

The decrease in yields of methane and ethane is due probably to the scavenging of methyl and ethyl radicals, which together with hydrogen radicals belong to the most active and have an important place in the propagation of the radical chain. An increased inner surface is advantageous not only for the energetically exacting initiation phase. For ethyl radicals, cleavage of a hydrogen radical with the formation of ethene cannot be excluded. Part of the methyl and ethyl radicals may be converted to methylene radicals. In an important secondary reaction, methylene radicals can react in the presence of a metal surface with steam to form carbon monoxide and hydrogen.

In the thermal decomposition of methylcyclohexane the following initiations are possible.



While the first three proceed through the chain mechanism, the last three produce biradicals, which decay and produce molecular products. From the first three alternatives (3a) to (3c) the alternative (3a) is energetically the most favorable, as the dissociation energy of the bond C-CH₃ varies between 326 and 334.4 kJ while that of the C-H bond is 392.9 to 401.3 kJ. The decomposition ac-

Table II. Retention Indices of Pyrolysis Products on a Capillary Squalane Column^a

	<i>I</i> ₅₀		<i>I</i> ₅₀		con- firmed by MS
	measd	tab. by R-C ^e	measd	tab. by R-C ^e	
1. methane					
2. ethane					
3. propene					
4. propane					
5. methylpropane					
6. 1,3-butadiene; 1-butene					
7. butane					
8. <i>trans</i> -2-butene	406.5	406.6	404.4	406.3	
9. <i>cis</i> -2-butene	416.5	416.9	416.5	417.3	
10. 1,2-butadiene	428.5	427.5 ^b	427.9	428.2 ^b	+
11. 3-methyl-1-butene	450.6	450.3	450.2	450.8	
12. 1,4-pentadiene	462.2	461.9 ^b	462.5	462.6 ^b	+
13. 2-methylbutane	474.9	475.3	474.5	475.5	
14. 1-pentene	481.6	481.8	482.0	481.8	
15. 2-methyl-1-butene	487.9	488.0	488.1	488.1	+
16. isoprene	497.6	499.2 ^b	497.5	499.3 ^b	+
17. pentane					
18. <i>cis</i> -2-pentene	505.0	504.9	505.7	505.1	
19. 1, <i>trans</i> -3-pentadiene	515.7	515.8	516.5	516.5	+
20. 1,3-cyclopentadiene	521.8	521.7 ^c			
21. 1, <i>cis</i> -3-pentadiene	524.4	524.2 ^b	525.1	525.4	+
22. 2,3-pentadiene	531.1	530.2			
23. cyclopentene	549.3	549.5			+
24. 3-methyl-1-pentene	551.8	551.4	553.0	551.9	
25. 4-methyl- <i>cis</i> -2-pentene	556.1	556.2	557.0	556.6	
26. 2,3-dimethyl-1-butene	558.4	558.8	559.4	559.6	
27. 4-methyl- <i>trans</i> -2-pentene	561.9	561.7			
28. 1,5-hexadiene	562.8	562.9	562.7	563.7	+
29. 2-methyl-1-pentene	580.1	580.1	579.8	580.6	
30. hexadiene	582.1		582.2		+
31. 1, <i>trans</i> -4-hexadiene	584.3	583.3 ^c			
32. 1, <i>cis</i> -4-hexadiene	587.2	586.9 ^b	587.5	587.8 ^b	
33. <i>trans</i> -3-hexene	592.1	592.1	591.7	591.6	
34. <i>trans</i> -2-hexene	596.9	596.9	596.7	596.7	
35. 2,3-dimethyl-1,3-butadiene	598.1	599.4 ^b	598.3	599.2 ^b	+
36. hexane					
37. 2-methyl-1, <i>cis</i> -3-pentadiene	603.3	600.9 ^c	602.9	601.9 ^c	+
38. 3-methylcyclopentene	605.5	604.2 ^c	606.5	608.2 ^c	+
39. 2-ethyl-1,3-butadiene	610.8	610.3 ^b	611.9	611.0 ^b	+
40. 1, <i>cis</i> -3-hexadiene	612.2	611.6 ^b	612.1	612.5 ^b	+
41. 1, <i>trans</i> -3-hexadiene	612.5	611.6 ^b			+
42. 2-methyl-1,3-cyclopentadiene	622.8	623.9 ^c			+
43. hexadiene	624.6		625.5		+
44. 1-methyl-1,3-cyclopentadiene	626.3	626.0 ^c			+
45. 2-methyl-1, <i>trans</i> -3-pentadiene	627.7	626.1 ^b	627.3	627.3 ^b	+
46. 4-methyl-1,3-pentadiene	629.6	627.5 ^b	628.7	628.6 ^b	
47. 4,4-dimethyl- <i>cis</i> -2-pentene	635.8	635.5	638.1	637.6	
48. benzene	637.4	637.2 ^d	642.2	642.0 ^d	+
49. 3-methyl-1, <i>trans</i> -3-pentadiene	640.7	640.7 ^b	643.5	642.5 ^b	+
50. 1-methylcyclopentene	644.5	644.5	646.5	646.8	+
51. 2,3-dimethyl-1-pentene	650.0	650.4	653.0	652.2	
52. 5-methyl-1-hexene	650.6	651.5 ^c			
53. 1,3-cyclohexadiene	652.8	654.7 ^c	653.4	659.1 ^c	+
54. 4-methyl- <i>trans</i> -2-hexene	657.4	656.7	657.5	657.4	
55. <i>cis</i> -2, <i>cis</i> -4-hexadiene	660.4	660.1 ^b	661.3	661.1 ^b	+
56. cyclohexane	662.7	663.9 ^b	663.9	668.3 ^b	+
57. 2-methylhexane	666.6	666.6	667.1	667.2	
58. 3,4-dimethyl- <i>cis</i> -2-pentene	669.7	670.6	670.3	671.5	
59. cyclohexene	671.0	670.9	675.7	675.7	+
60. 2-methyl-1-hexene	678.1	678.1	678.1	678.5	
61. 3,4-dimethyl- <i>trans</i> -2-pentene	679.4	678.3	679.9	678.8	
62. 1-heptene	681.8	681.8	682.2	682.3	+
63. 3-ethylpentene	686.3	686.0			
64. heptadiene	690.8		692.7		+
65. heptadiene	693.2		695.1		+
66. 3-ethyl-2-pentene	697.2	697.2			
67. <i>trans</i> -2-heptene	698.4	698.4	698.2	698.5	
68. heptane					
69. 2,3-dimethyl-2-pentene	703.1	703.4	703.5	704.2	
70. 3-ethylcyclopentene	712.4	712.4	716.6	715.8	+
71. vinylcyclopentane	717.6	718.6 ^c	713.8	715.0 ^c	
72. methylcyclohexane	725.8	726.9	731.5	730.6	+
73. 3-methylcyclohexene	730.6	730.7 ^b	735.7	735.7 ^b	+
74. 4-methylcyclohexene	733.2	733.1 ^b	738.1	738.4 ^b	+
75. 2-methyl- <i>trans</i> -3-heptene	741.1	741.1			

Table II (Continued)

	I_{50}		I_{50}		con- firmed by MS
	measd	tab. by R-C ^e	measd	tab. by R-C ^e	
76. 3,3-dimethylhexane	743.3	743.5			
77. toluene	745.2	745.5	750.0	750.0	+
78. 1-ethylcyclopentene	746.1	746.0 ^b			
79. norbornane	748.7	748.2 ^c	752.9	753.7 ^c	
80. 1-methylcyclohexene	761.7	761.6 ^b	766.0	766.1 ^b	+
81. dimethylcyclopentadiene	764.8				+
82. ethylenecyclopentane	766.9	768.9 ^c	770.3	771.4 ^c	+
83. cycloheptatriene	782.6		786.6		+
84. 1,cis-3-dimethylcyclohexane	784.9	785.0	789.7	789.9	+
85. octane					
86. 1,trans-2-dimethylcyclohexane	801.5	801.8	807.3	807.5	+
87. 1,trans-3-dimethylcyclohexane	805.3	805.6	810.5	810.8	+
88. 1,cis-2-dimethylcyclohexane	829.1	829.3	834.7	835.4	
89. ethylbenzene	834.1	833.6 ^d	839.5	838.9 ^d	+
90. <i>p</i> -xylene	848.3	848.2 ^d	853.4	853.3 ^d	+
91. <i>m</i> -xylene	850.5	850.4 ^d	855.7	855.3 ^d	+
92. styrene	860.9	862.9 ^c			+
93. <i>o</i> -xylene	868.9	868.7 ^d			+
94. nonane					

^a $l = 100$ m; i.d. = 0.25 mm; inlet pressure, 2.5×10^5 Pa; split ratio, 1:350; number of measurements, 4. ^b Data taken from Loewenguth and Tourres (1968). ^c Data taken from Hively and Hinton (1968). ^d Data taken from Soják and Ríjks (1976). ^e R-C = Ríjks and Cramers (1974).

Table III. Product Distribution in Pyrolysis Mixtures of Methylcyclohexane (mol/100 mol of Methylcyclohexane Decomposed)

	temp, °C							
	700	700	740	760	760	770	790	790
	conversion, %							
	4.51	20.87	12.02	26.70	48.93	24.54	30.62	51.69
methane	43.93	69.32	76.14	46.90	58.29	84.60	62.96	57.06
ethane	1.98	3.31	3.43	2.10	2.59	3.82	3.41	3.66
ethene	59.03	93.13	102.2	62.72	78.31	113.61	74.77	79.65
propene	17.55	47.40	37.12	22.55	30.36	36.88	29.43	31.63
methylpropene	3.35	8.81	9.04	3.51	4.21	6.23	4.68	4.47
1,3-butadiene	19.13	39.07	53.97	33.43	35.63	52.77	33.92	37.13
3-methyl-1-butene	0.59	0.69	1.24	0.54	0.35	0.80	0.29	0.42
1,4-pentadiene	0.39	0.76	0.83	0.20	0.35	0.93	0.34	0.39
isoprene	5.92	7.49	15.49	8.70	6.47	12.47	8.34	6.90
1,trans-3-pentadiene	3.15	3.40	7.59	3.51	2.54	4.56	2.60	2.53
1,cis-3-pentadiene	2.17	2.01	4.68	2.12	1.62	2.88	1.73	1.62
1,3-cyclopentadiene	0.59	1.24	3.32	2.17	3.14	4.09	2.41	2.75
2-methyl-1,3-cyclopentadiene	0.20	0.28	0.31	0.15	0.11	0.20	0.10	0.03
1-methyl-1,3-cyclopentadiene	0.39	0.41	0.10	0.30	0.21	0.40	0.20	0.10
3-methyl-1,trans-3-pentadiene	0.20	0.13	0.10	0.15	0.11	0.25	0.10	0.07
cyclohexane	0.79	0.49	1.97	0.69	0.53	1.21	0.48	0.35
1-methylcyclopentene	0.59	0.34	3.12	0.30	0.28	0.60	0.24	0.14
1,3-cyclohexadiene	0.39	0.55	1.45	0.54	0.85	1.21	0.77	0.77
4-methyl-trans-2-hexene	0.20	0.35	0.20	0.05	0.14	0.13	0.58	0.42
cyclohexene	9.66	1.17	9.77	5.34	1.73	6.37	2.70	1.44
1-heptene	1.38	0.83	3.11	2.17	0.88	1.61	1.40	0.70
benzene	0.99	2.98	6.97	3.95	7.64	7.57	6.56	5.56
3-methylcyclohexene	0.98	0.35	1.24	0.44	0.18	0.40	0.29	0.14
4-methylcyclohexene	3.15	1.11	5.19	2.17	1.02	2.34	2.02	0.88
1-methylcyclohexene	6.11	1.73	7.79	3.06	1.27	3.08	2.26	1.02
toluene	2.76	1.04	4.15	1.97	3.11	3.42	3.67	3.20
other hydrocarbons	11.10	27.61	12.18	8.15	7.8	14.39	9.75	15.68

cording to (3a) proceeds through methyl and cyclohexyl radicals. Methyl radicals may react with reactants, yielding methane and new radicals. Considering the relative stability of the six-membered ring, splitting of a C-H bond in the cyclohexyl radical may occur, resulting in the formation of cyclohexene and a hydrogen radical. Relatively high yields of cyclohexene indicate that this decomposition is preferred, which is in good agreement with the values of bond dissociation energies. The decomposition according to (3b) leads to methylcyclohexenes and toluene. However, the pyrolysis of individual methylcyclohexenes has shown that these are more prone to a deeper and more selective degradation than methyl-

cyclohexane (Bajus and Veselý, 1976b). The presence of the double bond favors not only splitting, but also dehydrogenations. The composition of the reaction product mixture shows that the double bond increases the selectivity of the conversion of 1-methylcyclohexene to ethene and isoprene and that of 3- and 4-methylcyclohexenes to propene and 1,3-butadiene. There is a relation between the yield of isoprene and 1-methylcyclohexene (Figure 13). The preferential degradation of 1-methylcyclohexene to isoprene indicates that the former product is an intermediate in the thermal decomposition of methylcyclohexane to isoprene. This cleavage proceeds most probably through a methylcyclohexenyl radical (reaction 4) or

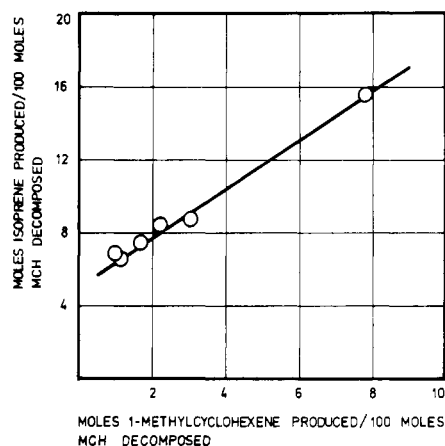
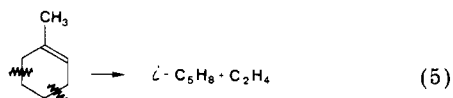
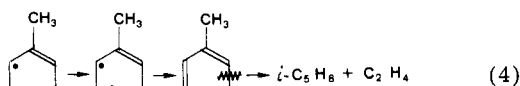
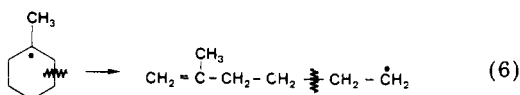


Figure 13. Product distribution of isoprene vs. product distribution of 1-methylcyclohexene.

through the breaking of a weakened bond in the β position to the double bond (reaction 5).



The initiation according to (3b) leads not only to dehydrogenations, but also to ring opening with production of ethene, methylbutene, and mainly isoprene (reaction 6).



In analogy to former reactions, it is possible to explain in case (3c) the production of propene, 1,3-butadiene, and pentadiene, in case (3d) the production of ethene, propene, butenes, and butadiene through intermediate heptenes, in case (3e) the production of the same products plus isobutene and isoprene; the same holds in case (3f), with methylbutenes, 1,3-pentadiene, 1,3-hexadiene, and methane in addition. The mechanism of the formation of the above and other products, e.g., cyclopentadiene and methylcyclopentadienes, was described previously (Bajus and Veselý, 1976a,b). Further attention will be devoted to reactions yielding products which are formed by splitting of methylcyclohexane and which have not been identified in our previous works. Some of them may be key intermediates. Their presence is only supposed as they are formed in minute amounts. They may give an indication whether the reaction is of homogeneous type or influenced by the inner surface.

The cleavage of ring C-C bonds in methylcyclohexane produces C_7 radicals. Further transformation proceeds not only by β splitting of C-C bonds, but also of C-H bonds. Therefore heptadienes are found in the reaction products. A fast isomerization of biradicals proceeds and heptenes are formed. A reaction of heptenyl radicals with the reactants cannot be excluded. Hydrogenations of intermediates, contractions and expansions of rings in cycloalkanes, and dehydrocyclizations of alkanes to 5-, 6-, and

7-membered rings may occur. Condensations of highly reactive components, e.g., butadienes and butenes, take place and hydrocarbons C_8 are formed. In the homogeneous phase, pure thermal reactions prevail. Metal walls enhance hydrogenations and dehydrogenations.

Conclusions

The increased surface of a tubular reactor in the pyrolysis of methylcyclohexane in the presence of steam influences the kinetic parameters and the selectivity of conversion.

The pyrolysis proceeds with a relatively low activation energy. The overall decomposition in a temperature range of 700 to 790 °C is a first-order reaction with a frequency factor of $0.532 \times 10^{11} \text{ s}^{-1}$ and an activation energy of 201.3 kJ mol⁻¹. The value of the rate constants is independent of the conversion of initial hydrocarbon.

The influence of the inner surface on the selectivity of the conversion of methylcyclohexane is reflected by lower yields of methane and ethane. High molecular reaction products and coke react under the catalytic influence of the wall with steam to give carbon monoxide and hydrogen. The formation of 1-methylcyclohexene as intermediate is important for the isoprene production. Based on detailed qualitative analysis by gas chromatography (tabulated data) and mass spectrometry, further reactions have been found to occur: hydrogenations, isomerizations, dehydrocyclizations, contractions and expansions of ring hydrocarbons, disproportionations, and condensations.

Nomenclature

A = frequency factor (Arrhenius plot), s⁻¹

A_F = reactant

E = activation energy, kJ mol⁻¹

k = first-order rate constant, s⁻¹

R = gas constant, J mol⁻¹ K⁻¹

R_i = product

S = inner surface of the reactor, cm²

S_w = steam

T = temperature, K

V = reactor volume, cm³

x = conversion of methylcyclohexane

Greek Letters

ϵ = relative volume change in the reaction

ν = moles of product formed per mole of methylcyclohexane decomposed

τ = residence time, s

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