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Pyrolysis of Organic Compounds Containing Long Unbranched Alkyl Groups

GEORGE W. MUSHRUSH AND ROBERT N. HAZLETT

*Combustion and Fuels Branch
Chemistry Division*

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NAVAL RESEARCH LABORATORY
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PYROLYSIS OF ORGANIC COMPOUNDS CONTAINING LONG UNBRANCHED ALKYL GROUPS

INTRODUCTION

Domestic oil-shale deposits are a tremendous resource as a potential source of liquid fuels. The proven recoverable oil-shale reserves far exceed those for petroleum. The oil-shale resource concentrated in three western states alone is estimated to be the equivalent of two trillion barrels of crude oil.

The U.S. Navy has been involved for some time in the development of Navy fuels from alternative sources such as oil shale [1-5]. As a part of this effort, the Naval Research Laboratory has been studying the effects of chemical composition on fuel properties, since such information will lead to a greater availability and better use of fuels [6-9].

JP-5 is a high-flash-point middle-distillate fuel for carrier-based jet aircraft. It must meet many exacting requirements for satisfactory performance [6]. One of the most stringent requirements is a low freezing point. It has been impractical to make JP-5 from some petroleum crudes, because it is difficult to meet the specification of a low freezing point (-47°C) and a high flash point (60°C) simultaneously.

The Naval Research Laboratory has related the freezing point of JP-5-type fuels to the n-alkane content, specifically n-hexadecane [7]. This relationship applies to jet fuels derived from any crude-oil source. In general, jet fuels made from shale crude have the highest n-alkane content, and those made from coal have the lowest n-alkane content.

The quantity of large n-alkanes (14%) present in shale crude is insufficient to explain the alkane content (up to 37%) of fuels derived from shale. Precursors to small straight-chain molecules in the jet fuel range might be branched or cyclic compounds containing long normal alkyl groups. When these compounds rupture during thermal refining, attack on a side chain could afford a path to an alkane.

Since the model compounds of this study are of the type that can be found in shale crude oil, the results of this study should be useful in explaining the observed products in shale-derived fuels and the thermal conditions under which they are formed.

The thermal cracking of hydrocarbons is well documented [10-14]. Rice [15] in 1933 proposed his now classical free-radical chain mechanisms of hydrocarbon pyrolysis. The thermal decomposition of small alkanes (C_1 through C_6) at low pressures and high temperatures is now well understood [16,17]. Although a few examples of thermal cracking of higher hydrocarbons are found in the literature [18,19], they are not adequate for detailed comparison. Most of these studies have a particular emphasis on kinetics within parameters of the Rice-Kossiakoff [13] theory. Fabuss, Smith, and Satterfield [18] have reported data and proposed a mechanism for n-hexadecane pyrolysis at pressures much higher than those studied by Rice.

The purpose of the present research is to test the validity of the Fabuss-Smith-Satterfield mechanism for lower temperatures and higher pressures and to report the product distribution for the thermal cracking of large model compounds of varied structure. These compounds were pyrolyzed at temperature and pressure conditions typical of the petroleum-refining process known as delayed coking.

EXPERIMENTAL DETAILS

Reagents

1-Phenyl pentadecane, 1-phenyl tetradecane, 2-methyl octadecane, and n-tridecyl cyclohexane were obtained from Pfaltz and Bauer and were passed through activated silica gel and fractionated. n-Hexadecane was a National Bureau of Standards reference sample and was used as received. 2-n-Pentadecyl pyridine was prepared by a standard method [20] and fractionated. The fraction boiling at 170°C at 33.2 Pa was retained and characterized by gas chromatography/mass spectrometry. The purity of the hydrocarbons was judged primarily from vapor-phase chromatography. The area of the main chromatogram peak was always >99.9% when compared to a similar compound used as an internal standard. Reagent-grade benzene was obtained from Fisher Chemical Co. The samples were stored in glass containers at 0°C.

Method

The compounds were all pyrolyzed at 723 K and about 600 kPa. A typical pyrolysis was carried out in a 15-cm-long, 6.4-mm-o.d. (1/4-inch-o.d.) 316 stainless-steel tube closed at one end and fitted at the other end with a stainless-steel valve via a Swagelok fitting. The tube, containing a weighed amount of sample (approximately 0.1 g), was attached to a vacuum system, cooled to 195 K, and subjected to three freeze-pump-thaw cycles. The deaerated samples were warmed to room temperature and pyrolyzed by inserting them into 7-mm holes in a 15-cm-diameter aluminum block fitted with heaters and a temperature controller. After the pyrolysis period, the tube was cooled to 195 K, and the valve was removed (unless the sample was analyzed for low-molecular-weight gases). Benzene (or other appropriate solvent) was added to the tube, which was then capped and warmed to room temperature. The solution and three subsequent rinses were transferred to a screw-cap vial (Teflon cap liner) and stored at 0°C until analysis. The sample concentration in the solvent was typically 5%. Prior to analysis, weighed amounts of internal standards were added. Since a typical chromatogram required 60 min, two internal standards were used. One afforded quantitation for the peaks with short retention times (typically p-xylene), and a second afforded quantitation for the peaks with longer retention times (typically 1-phenyl tridecane).

The stainless-steel tubes were used for several runs. All tubes were cleaned the same way. They were filled with toluene, cleaned with a stainless-steel brush, rinsed with toluene twice and then with methylene chloride, and dried in air at 723 K for 1 hour.

All samples were pyrolyzed for 15, 30, 60, 120, and 180 min. There was no evidence of catalysis by the tube walls except for n-tridecyl cyclohexane. Only conditioned tubes (as described) were used. A search of the literature gives several examples indicating that stainless steel below 823 K does not develop catalytic behavior [21,22]. Marschner [23] obtained the same results in stainless steel and Pyrex for the thermal cracking of n-octane when the walls of the tube were cleaned between runs with air or oxygen. Kunzru, Shah, and Stuart [24] found the catalytic behavior of stainless steel to be negligible in the cracking of nonane for the temperature range 923 to 1023 K.

The pyrolyzed samples were analyzed by three techniques, all based on gas chromatography. Peak identification for all three techniques was based on retention time matching with n-alkane and 1-alkene standards. In the first, a Hewlett-Packard model-5880A gas chromatograph with a flame ionization detector (FID) equipped with a 50-m wall-coated open tubular (OV-101) fused-silica capillary column gave the necessary resolution to distinctly separate the n-alkanes and 1-alkenes. A carrier gas flow of 1 ml/min was combined with an inlet split ratio of 60:1 and a temperature program with an initial hold at 50°C for 8 min, a ramp of 4°/min, and a final temperature of 275°C.

The second GC technique, used for longer-retention-time (C_{11} through C_{18}) n-alkanes and 1-alkenes, used a Perkin-Elmer model-3920B gas chromatograph equipped with an SE-30 33.5-m support-coated open tubular glass capillary column and an FID detector. The chromatogram was recorded and integrated on a Hewlett-Packard model-3390A reporting integrator. The temperature program was the same as for the 5880A analysis.

In the first technique the long retention times coupled with an inlet split did not give reliable analytical response above C_{12} . The p-xylene internal standard was consequently used for analysis of the C_5 through C_{10} hydrocarbons. The second GC technique was splitless and gave good response for longer retention times but not good separation at short retention times. The 1-phenyl tridecane internal standard was used for the C_{10} through C_{18} hydrocarbons. Both techniques gave the same analytical results for the midrange carbon numbers (C_7 through C_{12}). This served as a sensitive check between the two techniques.

In the third technique the gases formed during pyrolysis were analyzed using a Beckman model-GC-72-5 gas chromatograph equipped with an FID and a column packed with Apiezon L alumina. In this mode the column was operated at 200°C. The chromatogram was recorded and integrated on a Hewlett-Packard model-3390A reporting integrator. For this procedure, the tubes were cooled to 195 K after pyrolysis, and the tube valve was connected directly to a GC gas-sampling valve via a Swagelok connection. The sample tube was allowed to warm to room temperature before analysis. An external standard was used for calibration. A pressure gage measured the pressure in the sample loop at the time of analysis.

RESULTS

Figure 1 shows the chromatogram of the product from a 60-min pyrolysis of 2-methyl octadecane. It represents a typical chromatogram from the 5880A Hewlett-Packard gas chromatograph. The internal standards for this particular run were 1-phenyl propane and 1-phenyl pentadecane. Only 34.9% of the 2-methyl octadecane remains unreacted at this pyrolysis time. Table 1 lists the product identities along with corresponding retention times for aliphatic and branched C_5 through C_{18} hydrocarbons.

Table 2 lists, for each pyrolysis time, the sums of the n-alkanes and 1-alkenes for C_5 and higher aliphatics and the sums for all the substituted or branched hydrocarbons. Appendix A gives the detailed product distribution by carbon number and compound class for all compounds at each pyrolysis time. That is, entries in Table 2 are the totals of table columns in Appendix A.

For 1-phenyl pentadecane, 1-phenyl tetradecane, and 2-n-pentadecyl pyridine, the sums of n-alkane and 1-alkene yields are nearly equal for a 60-min pyrolysis. Short pyrolysis times favor 1-alkenes, and longer times favor n-alkane yields. The benzene-substituted alkenes from both 1-phenyl pentadecane and 1-phenyl tetradecane are quite stable, increasing from 3.6% and 2.7% for a 15-min stress to 8.1% and 9.0% for a 180-min stress. Styrene (C_2 in Tables A1b and A2b) is the alkene present in highest yield. For 1-phenyl pentadecane, styrene varies from 0.7% at 15 min to 7.8% at 180 min, and for 1-phenyl tetradecane, styrene increases from 0.5% at 15 min to 8.8% at 180 min.

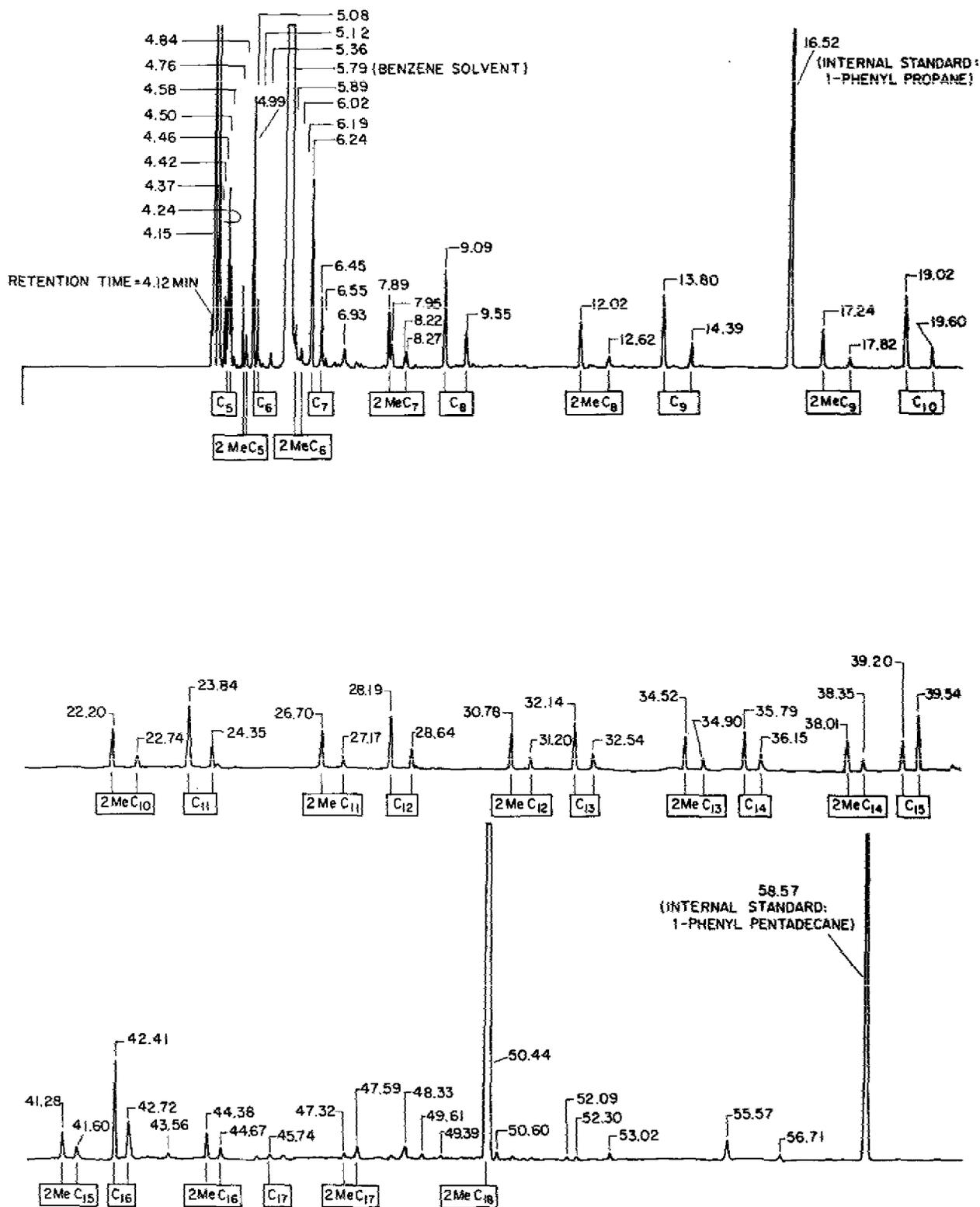


Fig. 1 — The chromatogram (cut into three pieces), from a Hewlett-Packard model-5880A gas chromatograph, of a 60-min pyrolysis of 2-methyl octadecane. The peaks occur in pairs, with the shorter-retention-time product being the alkene and the longer-retention-time product being the alkane.

Table 1 — Retention Times for a 60-Min Pyrolysis of 2-Methyl Octadecane from a Hewlett-Packard Model-5880A Gas Chromatograph

Carbon Chain Length	Retention Time (min)			
	Aliphatic Products		Branched (2-Methyl) Products	
	n-Alkane	1-Alkene	Alkane	Alkene
C ₁	—	—	—	—
C ₂	—	—	—	—
C ₃	—	—	—	—
C ₄	—	—	—	—
C ₅	4.50	4.46	4.84	4.76
C ₆	5.08	4.99	6.02	5.89
C ₇	6.45	6.24	8.27	7.89
C ₈	9.55	9.09	12.62	12.02
C ₉	14.39	13.80	17.82	17.24
C ₁₀	19.60	19.02	22.74	22.20
C ₁₁	24.35	23.84	27.17	26.70
C ₁₂	28.64	28.19	31.20	30.78
C ₁₃	32.54	32.14	34.90	34.52
C ₁₄	36.15	35.79	38.35	38.01
C ₁₅	39.54	39.20	41.60	41.28
C ₁₆	42.72	42.41	44.67	44.38
C ₁₇	—	45.74	47.59	47.32
C ₁₈	—	—	50.44	—

Table 2 — Alkane and Alkene Yields From Pyrolysis

Time (min)	Yield of the Hydrocarbon Products (%)						Not Reacted (%)
	Aliphatic*		Substituted		Branched		
	n-Alkane	1-Alkene	Alkane	Alkene	Alkane	Alkene	
Pyrolysis of 1-Phenyl Pentadecane							
15	4.4	10.1	8.1	3.6			62.5
30	5.1	13.1	11.7	4.9			35.0
60	9.5	9.9	20.9	4.6			8.7
120	9.6	7.0	17.5	6.1			3.0
180	9.7	3.8	15.1	8.1			1.0
1-Phenyl tetradecane							
15	2.8	8.2	7.1	2.7			64.0
30	5.8	12.9	14.1	4.6			35.4
60	9.0	10.4	19.6	5.9			7.2
120	9.3	8.7	20.7	6.9			4.5
180	9.5	3.4	18.0	9.0			1.4
2-n-Pentadecyl Pyridine							
15	5.2	7.8	6.4	2.7			53.5
30	10.5	9.1	12.8	3.6			25.4
60	10.9	10.9	15.8	0.2			12.0
120	10.1	6.9	18.1	0.0			3.3
180	7.4	3.3	18.6	0.0			0.1
2-Methyl Octadecane							
15	0.7	1.9			0.9	0.1	77.1
30	2.8	6.9			1.2	3.5	56.6
60	9.0	12.3			2.3	6.0	34.9
120	12.3	6.6			4.1	3.9	8.0
180	6.9	6.6			1.7	3.1	4.7
n-Tridecyl Cyclohexane							
15	0.1	0.1	0.6	0.1			87.3
30	4.9	8.7	3.5	5.6			79.6
60	6.1	10.7	3.7	6.2			42.0
120	9.6	9.6	6.4	4.2			12.6
180	9.4	6.2	6.2	2.6			3.7
Hexadecane							
15	0.2	1.8					95.1
30	2.3	10.8					75.9
60	10.3	17.6					33.6
120	12.9	14.9					17.5
180	22.1	10.6					5.7

*Does not include C₁ through C₄ values.

Toluene and ethyl benzene were the most stable phenyl alkanes formed. For a 15-min pyrolysis of 1-phenyl pentadecane, 3.3% toluene and 2.9% ethyl benzene were formed. At 180 min, 14.9% and 0.2% respectively were formed. The same trend was noted for 1-phenyl tetradecane: at 15 min the toluene yield was 3.2% and the ethyl benzene yield was 2.4%. At 180 min 14.4% and 0.2% respectively were found. Ethyl benzene was a major initial product, but it does break down at long stress times. No benzene was found.

The pyridine substituted alkenes from 2-n-pentadecyl pyridine show a remarkable dissimilarity with all of the other compounds pyrolyzed. The pyridine substituted alkenes exhibit little thermal stability after a pyrolysis of only 30 min, and the low yield drops to zero. The pyridine substituted alkanes, however, show a high degree of stability, gradually increasing in yield until at 180 min the products total 18.6%. The most stable of the substituted pyridines was 2-methyl pyridine, which increased from 3.0% at 15 min to 11.7% at 180 min (Table A3b). No pyridine was found.

Table 3 lists, for the 60-min pyrolysis for the compounds reacted, the total aliphatic product yields (C_1 and higher). Table 4 shows, for the 60-min pyrolysis for the compounds stressed, the yields of the individual C_1 through C_4 n-alkane and 1-alkene hydrocarbons.

That substituted pyridines and benzenes are much more susceptible to pyrolysis can be seen by a comparison with n-hexadecane. For a 15-min pyrolysis, 62.5% of the 1-phenyl pentadecane, 64.0% of 1-phenyl tetradecane, and only 53.1% of 2-n-pentadecyl pyridine remain, but 95.1% of the n-hexadecane remains (Table 2). For a 60-min pyrolysis the C_1 through C_4 yield for n-hexadecane was only 4.8% (Table 4). The same product trend is observed for the n-hexadecane as for the other compounds: the n-alkane does not equal the 1-alkene yield until approximately the 120-min pyrolysis (Table 2). At 180 min the n-alkanes predominate. Under the noncatalytic conditions of the experiment, isomerization was not expected, and only slight traces of isomerization were found. At 180 min for the n-hexadecane, the lower n-alkanes and 1-alkenes predominate, with the n-pentane value being 9.6% and the 1-pentene value being 5.0% (Table A6). Figure 2 shows the decrease in the long-chain compounds and the concomitant dramatic increase in the shorter chain hydrocarbons as the pyrolysis time increases beyond 60 min for n-hexadecane.

The pyrolysis of 2-methyl octadecane is faster than that of n-hexadecane. During pyrolysis of the 2-methyl octadecane 77.1% remains at 15 min versus 56.6% at 30 min, which compares to 95.1% and 75.9% respectively for the n-hexadecane (Table 2). The yield of the straight-chain hydrocarbons from 2-methyl octadecane exceeded that of the branched hydrocarbons by 2- to 3-fold (Table 3).

Substituted cyclohexanes would be expected to be considerably more reactive than straight-chain hydrocarbons. This was not the case, however. For a 15-min pyrolysis, 87.3% of the n-tridecyl cyclohexane remains. The product distribution is as expected, but the n-alkane yield does not approximate the 1-alkene yield until 120 min of pyrolysis. The long-chain cyclohexane also produced the lowest C_1 through C_4 yield (4.1%) for the 60-min stress.

The substituted benzenes and pyridines did not yield either benzene or pyridine. However, n-tridecyl cyclohexane yielded cyclohexane as well as benzene, toluene, and methyl cyclohexenes in appreciable concentrations. For example, a 180-min pyrolysis yields 5.3% cyclohexane and 2.5% toluene.

Table 3 — Total Alkane and Alkene Yields from a 60-Minute Pyrolysis

Carbon Numbers	Yield of the Hydrocarbon Products (%)					
	Aliphatic		Substituted		Branched	
	n-Alkane	1-Alkene	Alkane	Alkene	Alkane	Alkene
Pyrolysis of 1-Phenyl Pentadecane						
C ₁ and higher (in Table 2)*			20.9	1.6		
C ₅ and higher (in Table 2)	9.5	9.9				
C ₁ through C ₄ (not in Table 2)	7.3	6.4				
Total	33.1		25.0			
1-Phenyl Tetradecane						
C ₁ and higher*			19.6	5.9		
C ₅ and higher	9.0	10.1				
C ₁ through C ₄	6.9	6.2				
Total	32.5		25.5			
2-n-Pentadecyl Pyridine						
C ₁ and higher*			15.8	6.2		
C ₅ and higher	10.9	10.9				
C ₁ through C ₄	9.1	7.0				
Total	37.9		16.0			
2-Methyl Octadecane						
C ₅ and higher	9.0	12.3			2.3	6.0
C ₁ through C ₄	5.6	4.9				
Total	31.8				8.3	
n-Tridecyl Cyclohexane						
C ₁ and higher*			3.7	6.2		
C ₅ and higher	6.1	10.7				
C ₁ through C ₄	2.6	1.5				
Total	20.9		9.9			
n-Hexadecane						
C ₅ and higher	10.3	17.6				
C ₁ through C ₄	2.9	1.9				
Total	32.7					

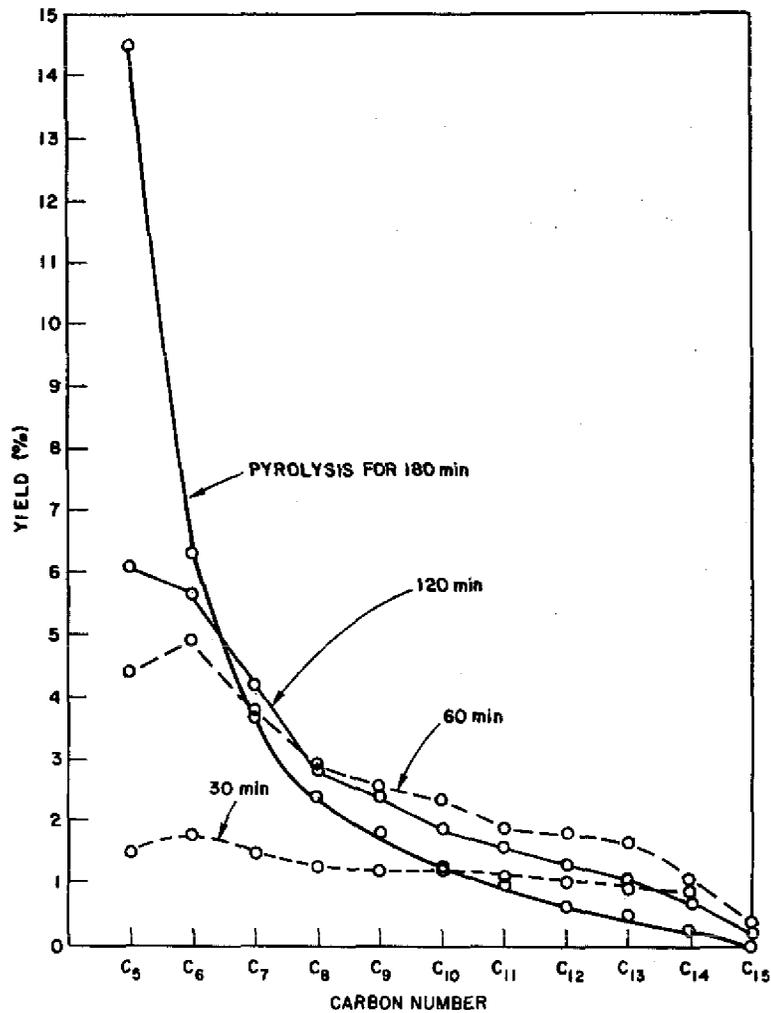
*Carbon number of the side chain.

Table 4 — C₁ Through C₄ n-Alkane and 1-Alkene Yields from a 60-Minute Pyrolysis

Compound Pyrolyzed	Yield of the Hydrocarbon Product (%)										Total
	n-Alkane					1-Alkene					
	C ₁	C ₂	C ₃	C ₄	Total*	C ₁	C ₂	C ₃	C ₄	Total*	
1-Phenyl pentadecane	1.2	3.0	2.1	1.0	7.3	—	2.8	2.2	1.4	6.4	13.7
1-Phenyl tetradecane	1.1	2.9	2.0	0.9	6.9	—	2.7	2.2	1.3	6.2	13.1
2-n-Pentadecyl pyridine	1.0	3.2	3.8	1.1	9.1	—	1.9	3.8	1.3	7.0	16.1
2-Methyl octadecane	0.6	1.5	3.0	0.5	5.6	—	1.0	2.1	1.8	4.9	10.5
n-Tridecyl cyclohexane	0.5	1.3	0.6	0.2	2.6	—	0.7	0.6	0.2	1.5	4.1
n-Hexadecane	0.3	1.2	1.0	0.4	2.9	—	0.5	1.0	0.4	1.9	4.8

*Value that was given in Table 3.

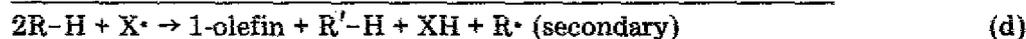
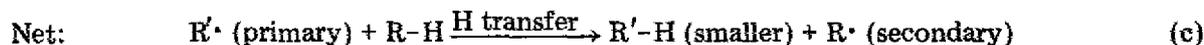
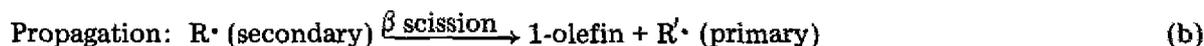
Fig. 2 — Yield of n-alkanes plus 1-alkenes from the pyrolysis of n-hexadecane



A material balance was run for each compound. The main peaks of the chromatograms account for approximately 85% of the original compounds. The small peaks account for another 5 to 6%. It is inferred that the remainder is either polymerized or present as char. The formation of insolubles was not noticeable for short pyrolysis times. A small amount of insolubles was noted for the 120- and 180-min pyrolysis times, especially for 2-n-pentadecyl pyridine. The product distribution was repeatable to 2% for each component regardless of whether a new stainless-steel tube or a previously used but conditioned tube was used.

DISCUSSION

When pyrolyzed at high temperature and low pressure, hydrocarbons are broken down to small olefins by the Rice free-radical mechanism. Fabuss-Smith-Satterfield (FSS) behavior [18] occurs at conditions (lower temperature and higher pressure) more typical of shale retorting and delayed coking. In FSS behavior a single fragmentation step occurs which results in approximately equal amounts of n-alkanes and 1-olefins of intermediate chain length. The FSS sequence can be pictured as follows:



The secondary radical formed can undergo β scission or termination. The ratio of the rates of b and e determine the length of the free-radical chain. At the high pressure of this system, intermolecular hydrogen transfer (c) predominates over intramolecular hydrogen transfer, which is a key step in the Rice pyrolysis regime.

Predictions of FSS behavior are followed for all the compounds pyrolyzed. The first members of the n-alkane and 1-olefin series are formed in smaller amounts than the second members. Low n-tetradecane (0%), n-pentadecane (0%), and 1-pentadecene (0.2%) yields follow traditional FSS theory, for a 30-min stress of n-hexadecane (Table A6). The model also predicts equal amounts of hydrocarbons in the intermediate chain-length range, a behavior observed for several compounds in these experiments at the shorter pyrolysis times.

The effect of pyrolysis time on yield for n-hexadecane is illustrated in Fig. 2. The sum of the n-alkane and the 1-alkene yields for each carbon number is plotted. For a 30-min stress of n-hexadecane, C_8 through C_{14} products are approximately equal in concentration. Consequently one-step FSS pyrolysis is rate controlling. The total yield increases at 60 min, but the shift to lower carbon numbers (C_5 through C_7) indicates that products are forming and then undergoing secondary decomposition. This trend is extended significantly at longer times, such as is shown by the 180-min stress data, with C_5 reaching a 14.6% yield.

The situation for pyrolysis of aromatic substituted alkanes is different. Pyridine and benzene rings greatly enhance free-radical formation. For example, the percentage of 2-n-pentadecyl pyridine decomposed in 30 min (indicated in Table 2 by the percentage not reacted) is not matched by the

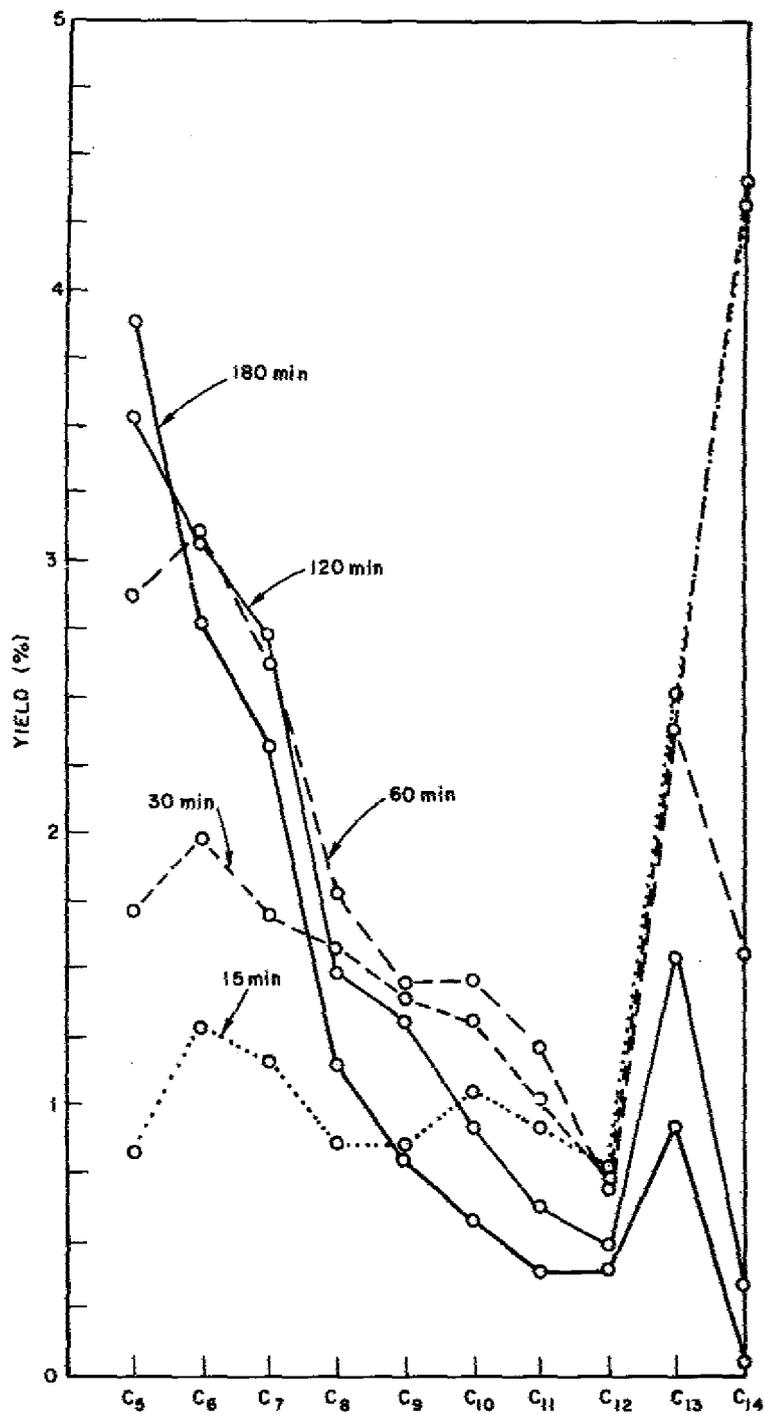


Fig. 3 — Yield of n-alkanes plus 1-alkenes from the pyrolysis of 1-phenyl pentadecane

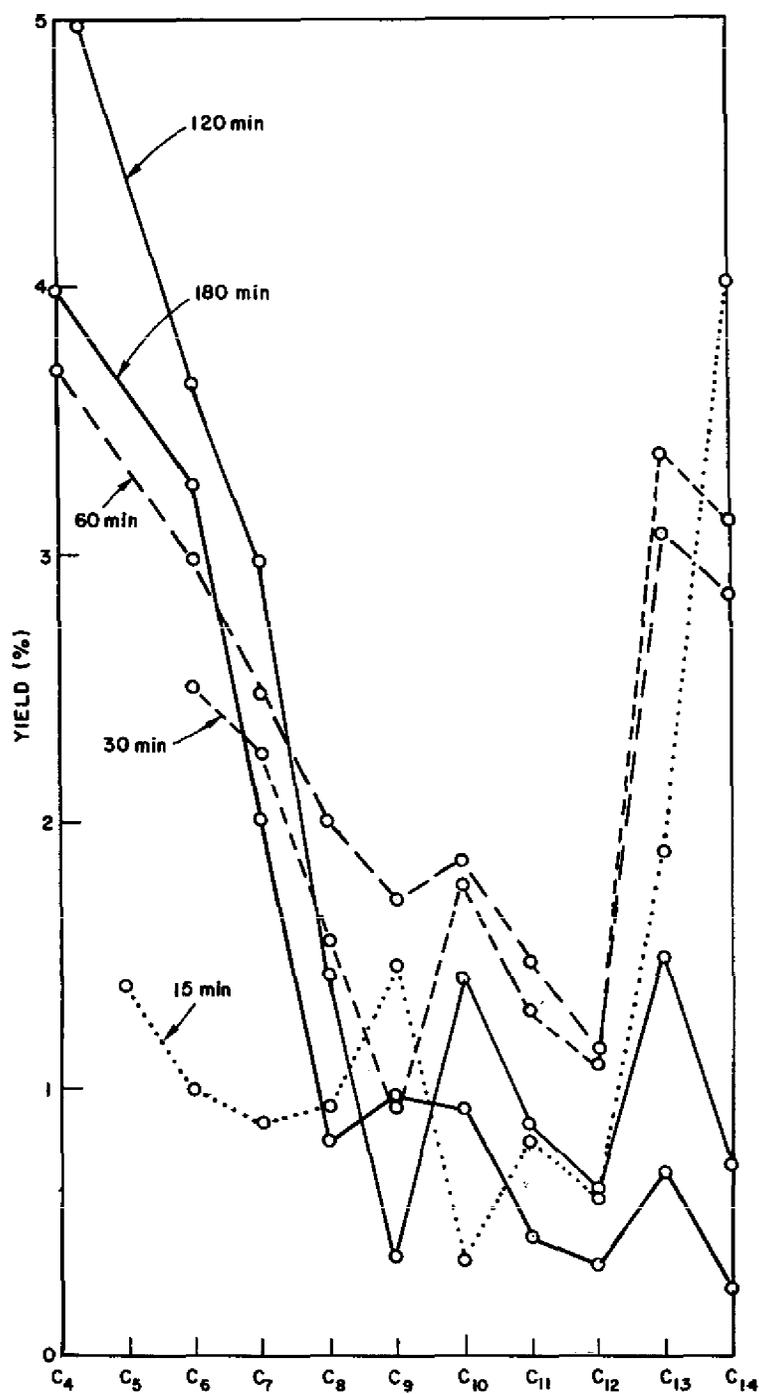
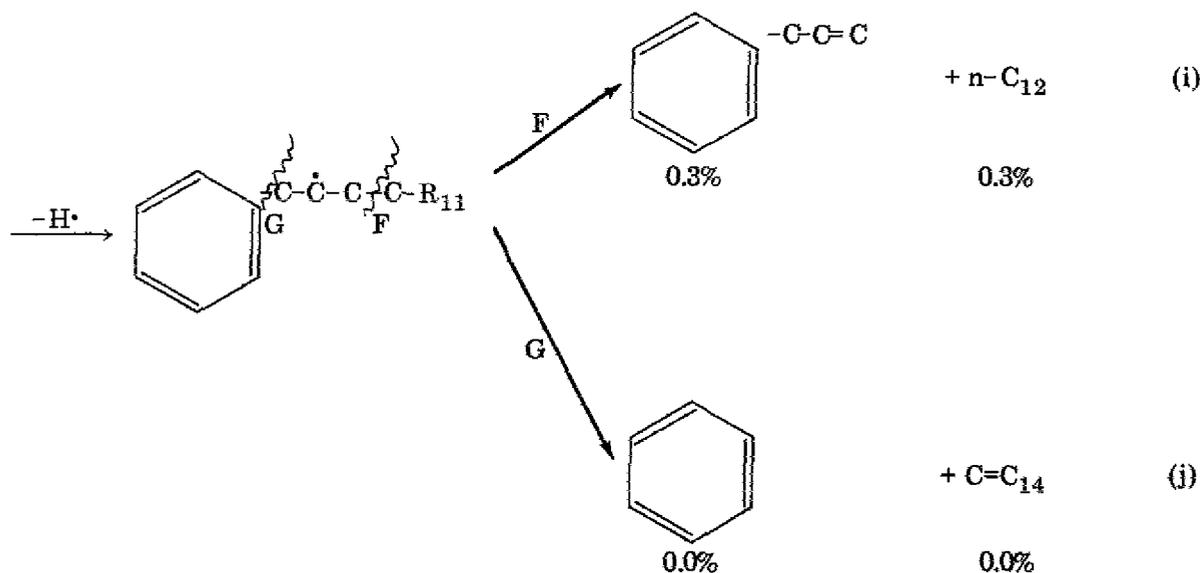


Fig 4 — Yield of n-alkanes plus 1-alkenes from the pyrolysis of 2-pentadecyl pyridine



The same mechanism as pictured would apply for a long-chain substituted pyridine.

Bond-scission reactions initiate (or are the first steps in) the mechanisms of the thermal pyrolysis of hydrocarbons.

The substituted benzenes produced in steps f to j all form thermally via free radicals: the radical in step f, the γ radical in steps g and h, the β radical in steps i and j, and the radicals on all other carbons of the alkane side chain. This is followed by β scission, resulting in the product mix shown for steps f through j.

Step f requires that the bond break at position A, position B, or both. As pictured, when the bond breaks at position A styrene and n-tridecane result. Styrene is stable toward pyrolysis at the temperatures of this study, and its yield undergoes a steady buildup, approaching 7.8% at the 180-minute pyrolysis. The n-tridecane is not thermally stable and subsequently decreases in yield with increasing pyrolysis. It is unstable because of secondary cracking reactions, yielding lower n-alkanes and 1-alkenes. No ring opening was observed, as would be required by the bond breaking at position B.

In steps g and h the γ free radical is depicted. Beta scission results in toluene and 1-tetradecene. Reaction path D (step g) predominates, because the scission via this path results in the very stable benzyl free radical forming.

According to the theory of chain inhibition, stabilized free radicals do not initiate chain reactions and therefore can recombine only with one another [25]. This recombination of benzyl radicals was not observed in any of the chromatograms. However, at temperatures of 673 K and above, stabilized radicals like benzyl can abstract hydrogen from hydrocarbons and therefore can initiate chain processes [26]. Pyrolysis studies at temperatures of 673 K and above have shown chain decomposition of short-chain alkyl benzenes even in the presence of large amounts of added inhibitors [27,28]. The low product yield of step h (scission at position E) for a 15-min stress or at any other pyrolysis time shows the marked stability of the benzyl radical. Other small alkyl benzenes formed will all subsequently undergo secondary pyrolysis, as can be seen from the product tabulation in Appendix A.

Bond scission at position G (step j) was not a viable reaction step. The yield of both benzene and 1-pentadecene at any pyrolysis time was zero. In pyrolysis studies of short-chain alkyl benzenes (C_2 and C_3), no benzene was observed in the product mix [29,30].

The free radical can be formed randomly on any carbon of the side chain, as can be seen in the product breakdown in Appendix A. Although most substituted benzenes are observed at a short pyrolysis time, toluene predominates at all pyrolysis times, indicating that the gamma position is the most vulnerable to pyrolysis and that with increasing pyrolysis time secondary pyrolysis steps are of major importance.

As shown in Appendix A, the pyridine substituted alkenes are formed in considerable yield at short pyrolysis times, but after 30 min the olefin concentration drops to zero. The pyridine substituent enhances the free-radical breakdown of the olefin. This is not a dramatic for the benzene derivatives. The substituted olefins decrease but do not approach zero until 180 min of pyrolysis. As pyrolysis times increase, the substituted alkanes decrease in chain length, with 2-methyl pyridine and 2-ethyl pyridine ultimately being the major products. With the benzenes, toluene and styrene are the major products at longer pyrolysis times.

For 1-phenyl pentadecane, toluene increases from 3.3% at a 15-min stress to 14.9% for a 180-min stress (Table A1b). For 1-phenyl tetradecane, the toluene yield increases from 3.2% at 15 min to 14.8% for a 120-minute stress (Table A2b). The steady buildup of the toluene yield is reasonable, since toluene has been found to be extremely resistant to pyrolysis at temperatures below 1173 K [31]. It is, however, quite reactive in the temperature range from 1473 to 1773 K. These temperatures far exceed any in the present study. This thermal stability is not displayed by any of the other longer chain substituted benzenes.

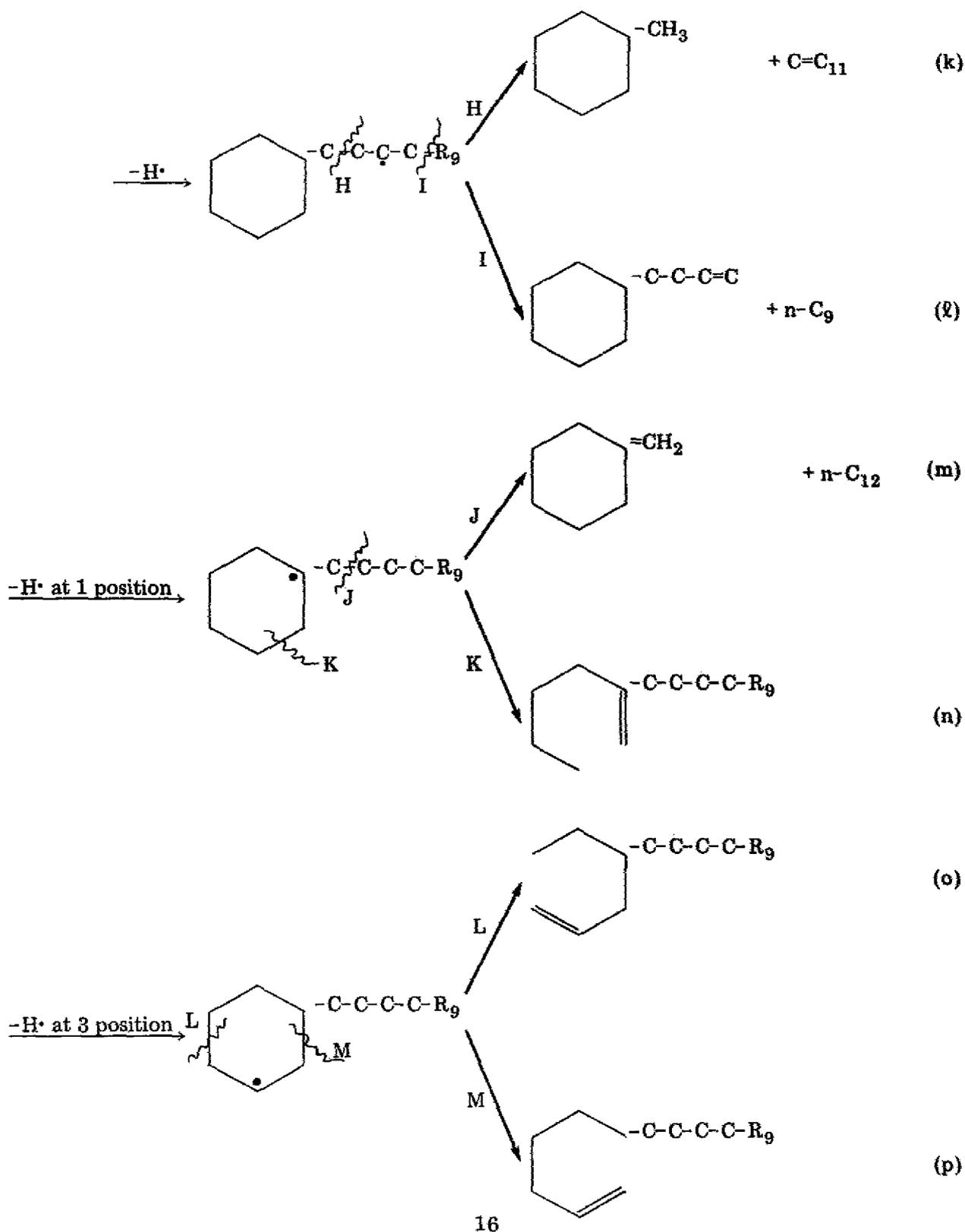
For 2-n-pentadecyl pyridine, only two substituted pyridines (2-methyl and 2-ethyl) were found to be pyrolysis resistant under these experimental conditions (Table A3b).

The C_1 through C_4 aliphatic product distribution was determined for the 60-min pyrolysis. This was the stress time at which the sum of the n-alkane and 1-alkene yields was maximized. Table 3 gives the C_1 and higher yields of the n-alkanes and 1-alkenes. The C_1 through C_4 yield was $9.1 + 7.0 \approx 16\%$ for the pyridine and 13 to 14% for the benzenes. The C_2 and C_3 yields are approximately equal (2 to 3%). The total n-alkane plus 1-alkene yield was 33.1% for 1-phenyl pentadecane, 32.5% for 1-phenyl tetradecane, and 37.9% for 2-n-pentadecyl pyridine.

2-Methyl octadecane was found to be significantly less reactive than the pyridine or benzene substituted alkanes. It is more reactive than the n-hexadecane. This is reasonable, since the product distribution of 2-methyl octadecane could be explained by the preferential attack on the tertiary hydrogen, the weakest C-H bond. The total product distribution (C_1 and up) was quite similar to that of the n-hexadecane.

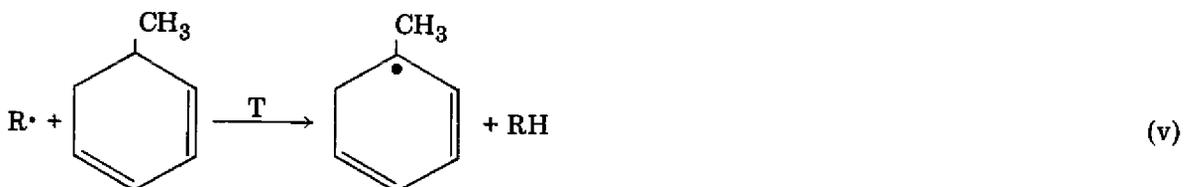
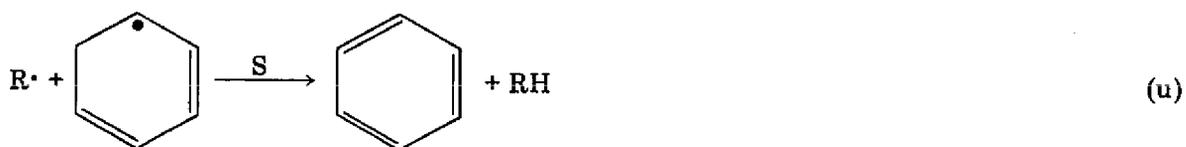
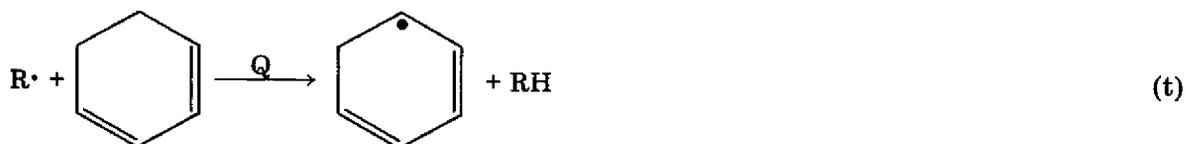
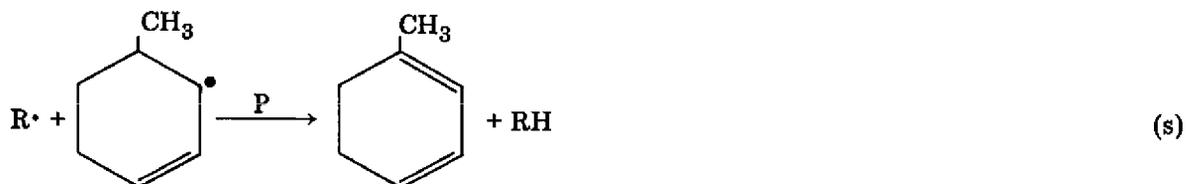
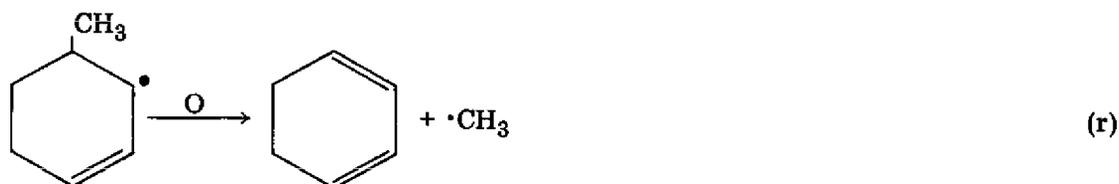
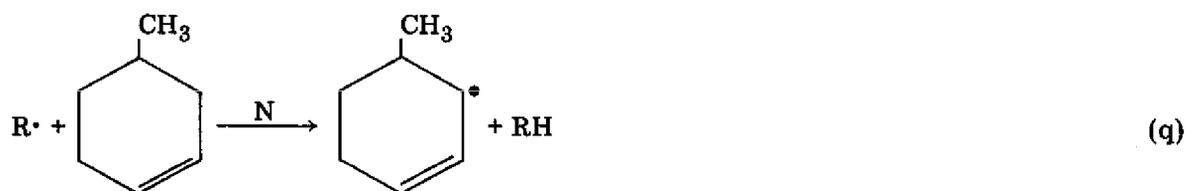
Substituted cyclohexanes would be expected to be less reactive than either the pyridines or the benzenes. Surprisingly, it was also less reactive than n-hexadecane or 2-methyl octadecane at pyrolysis times of 60 min and less. The products besides the n-alkanes and 1-alkenes include toluene, benzene, and methyl cyclohexenes. The lower than expected conversion is due to self-inhibition by the methyl cyclohexenes. Cyclohexene has been used by several authors as a free-radical scavenger [32,33]. At short pyrolysis times the methyl cyclohexene starts a steady buildup. As its concentration increases, aromatic compounds begin to appear. It would seem that these aromatic compounds are the secondary products which are formed from the decomposition of the substituted cyclohexenes. That toluene was the only substituted benzene formed is not surprising when one considers its stability and the observed toluene yield from the pyrolysis of the 1-phenyl pentadecane.

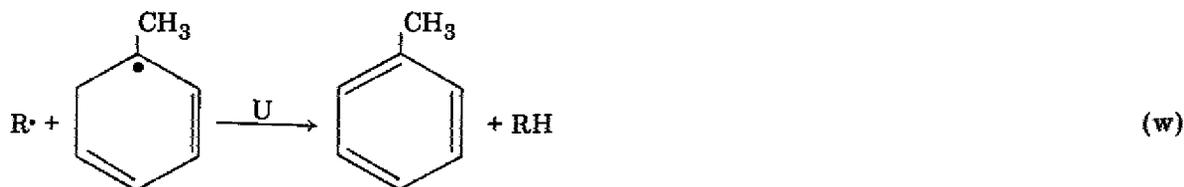
For the long-chain cyclohexanes a pyrolysis mechanism similar to that of the benzenes can be pictured:



Steps k and l can be rationalized in a similar way as those for the benzenes, with random β scission on the side chain leading to smaller n-alkanes and 1-alkenes and shorter chain cyclohexanes (both alkanes and alkenes). The ring could also undergo attack (1, 2, or 3 position). The products that would result by β scission within the ring are illustrated by attack at positions K, L, and M. The products formed by the attack are illustrated by steps n, o, and p. None of the products depicted by these steps (or those by attack on the 2 position) are observed on any of the chromatograms. It is possible that attack on the ring does occur with the smaller substituted cyclohexanes that are formed in the pyrolysis scheme. But it is unlikely to contribute to the product mix to more than a slight degree, since isomers of the type formed in steps o and p are not detected on the chromatograms. However, step p for a short-chain cyclohexane would yield a small 1-alkene that would be indistinguishable from the same small 1-alkene resulting from β scission on the side chain.

Reactions that could account for the aromatic formation from a substituted cyclohexene would be





The benzene derivatives could be formed by the radical attack on a diene (step t) or by the questionable direct molecular elimination of hydrogen. The benzene concentration remains relatively low compared to that of toluene. This would indicate that mechanism steps such as steps t and u are not as favorable as steps v and w. These reactions of the cyclohexenes are known to be surface catalyzed [30], and undoubtedly this catalysis accounts for the change in the product distribution noted at long pyrolysis times.

SUMMARY

The formation of n-alkanes in the jet-fuel distillation range can be explained if large n-alkanes are present in the crude-oil source. Quantities of large n-alkanes present are insufficient, however, to explain the amounts found (up to 37%) in the jet fuel made from shale crudes. Other possible precursors to small straight-chain molecules are branched compounds or substituted cyclic compounds.

The compounds pyrolyzed in this study were 1-phenyl pentadecane, 1-phenyl tetradecane, 2-n-pentadecyl pyridine, 2-methyl octadecane, 1-cyclohexyl tridecane, and n-hexadecane.

Product trends were similar for all compounds stressed. Short pyrolysis times (15 min) favor the yield of 1-alkenes, and longer pyrolysis times (180 min) favor an increased n-alkane production.

Pyridine and benzene rings greatly enhance free-radical formation. For example, the percent of 2-n-pentadecyl pyridine decomposed in 30 min of pyrolysis is not matched by the n-hexadecane until almost 120 min. The total yield of product, 36%, for 2-n-pentadecyl pyridine is not attained by n-hexadecane at even 180 min of pyrolysis. A similar trend was noted for the phenyl alkanes.

The most stable substituted benzenes formed were toluene and styrene. For 1-phenyl pentadecane, toluene increased in yield from 3.3% at 15 min of pyrolysis to 14.9% at 180 min, and styrene increased in yield from 0.7% at 15 min to 7.8% at 180 min. No benzene was found.

For the substituted pyridines, only 2-methyl pyridine was formed in appreciable concentration, 3.0% at 15 min of pyrolysis and increasing to 11.7% at 180 min. No pyridine was found. The results for substituted benzenes and pyridines are consistent with primary attack at the alpha and gamma positions.

Substituted cyclohexanes would be expected to be less reactive than either the pyridines or the benzenes. Surprisingly, 1-cyclohexyl tridecane was also less reactive than either n-hexadecane or 2-methyl octadecane at pyrolysis times of 60 min and less. The products for the pyrolysis of 1-cyclohexyl tridecane besides the alkanes and alkenes include benzene, toluene, and methyl cyclohexenes. The lower than expected conversion is due to self-inhibition by the methyl cyclohexenes.

When pyrolyzed at high temperature and low pressure, hydrocarbons are broken down to smaller olefins by the Rice free-radical mechanism. Fabuss-Smith-Satterfield (FSS) behavior

occurs at conditions (lower temperature and higher pressure) more typical of shale retorting and delayed coking. In FSS behavior a single fragmentation step occurs which results in approximately equal amounts of n-alkanes and 1-alkenes of intermediate chain length. The major initial product distribution can be explained on the basis of FSS theory for all of the compounds pyrolyzed.

The report shows that attack in the side chain of model compounds typically found in shale crudes affords a path to significant yields of n-alkanes.

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Appendix A

PRODUCT DISTRIBUTION FROM THE PYROLYSIS OF 1-PHENYL PENTADECANE,
1-PHENYL TETRADECANE, n-TRIDECYL CYCLOHEXANE, 2-METHYL OCTADECANE,
2-PENTADECYL PYRIDINE, AND n-HEXADECANE

Table A1a — Yield of n-Alkanes and 1-Alkenes from Pyrolysis of 1-Phenyl Pentadecane.
For accentuation the yield values of 1.0% or more are enclosed by rectangles.

Carbon Number	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	n-al-kane	1-al-kene								
C ₅	0.3	0.5	0.7	1.0	1.6	1.3	2.3	1.3	2.9	1.0
C ₆	0.3	1.0	0.4	1.5	1.2	1.9	1.5	1.6	1.8	1.0
C ₇	0.4	0.8	0.5	1.2	1.3	1.4	1.5	1.3	1.6	0.7
C ₈	0.3	0.6	0.5	1.1	0.8	1.0	0.8	0.7	0.9	0.3
C ₉	0.3	0.6	0.4	1.0	0.7	0.8	1.0	0.5	0.7	0.2
C ₁₀	0.3	0.8	0.3	1.0	0.7	0.8	0.4	0.6	0.5	0.1
C ₁₁	0.1	0.8	0.1	0.9	0.5	0.8	0.4	0.3	0.3	0.1
C ₁₂	0.3	0.5	0.2	0.5	0.4	0.3	0.2	0.3	0.2	0.2
C ₁₃	2.0	0.5	1.9	0.5	2.2	0.2	1.4	0.1	0.8	0.2
C ₁₄	0.1	4.0	0.1	4.4	0.1	1.4	0.1	0.3	—	—

Table A1b — Yield of Substituted Alkanes and Alkenes from Pyrolysis of 1-Phenyl Pentadecane.
Double rectangles accentuate values from 5.0 to 9.9%, and triple rectangles accentuate values of 10.0% or more.

Carbon Number of Side-Chain	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene
C ₁	3.3	—	6.3	—	10.9	—	13.3	—	14.9	—
C ₂	2.9	0.7	3.1	1.8	5.6	3.3	0.6	6.1	0.2	7.8
C ₃	0.1	0.3	0.2	0.3	0.8	0.2	1.2	0.1	1.4	—
C ₄	0.3	—	0.5	—	0.9	0.1	1.0	—	0.8	—
C ₅	0.2	0.3	0.2	0.4	0.7	0.1	0.6	—	0.4	0.1
C ₆	0.2	0.4	0.2	0.4	0.4	0.1	0.3	—	0.2	0.1
C ₇	0.1	0.3	0.2	0.4	0.3	0.2	0.2	0.2	0.2	0.1
C ₈	0.2	0.3	0.2	0.3	0.3	0.1	0.1	—	0.2	—
C ₉	0.2	0.3	0.2	0.3	0.3	0.1	0.1	—	0.1	—
C ₁₀	0.2	0.3	0.2	0.3	0.2	0.1	0.1	—	—	—
C ₁₁	0.2	0.3	0.2	0.3	0.2	0.1	—	—	—	—
C ₁₂	0.2	0.2	0.2	0.2	0.2	0.1	—	—	—	—
C ₁₃	—	0.2	—	0.2	0.1	0.1	—	—	—	—

Table A2a — Yield of n-Alkanes and 1-Alkenes from Pyrolysis of 1-Phenyl Tetradecane

Carbon Number	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	n-al-kane	1-al-kene								
C ₅	0.2	0.5	0.7	1.0	1.7	1.6	2.1	1.5	2.7	0.8
C ₆	0.2	0.9	0.6	1.8	1.3	2.3	1.5	2.1	1.8	0.9
C ₇	0.3	0.7	0.6	1.3	1.2	1.6	1.4	1.3	1.6	0.7
C ₈	0.2	0.5	0.5	1.0	0.9	1.2	0.9	1.0	1.0	0.3
C ₉	0.2	0.7	0.4	1.1	0.8	1.0	0.9	0.7	0.7	0.2
C ₁₀	0.2	0.9	0.3	1.3	0.5	0.9	0.5	0.9	0.4	0.1
C ₁₁	0.2	0.5	0.4	0.7	0.5	0.5	0.5	0.3	0.3	0.1
C ₁₂	1.2	0.4	2.2	0.6	2.0	0.2	1.4	0.2	1.0	0.1
C ₁₃	0.1	3.1	0.1	4.1	0.1	1.1	0.1	0.6	—	0.2

Table A2b — Yield of Substituted Alkanes and Alkenes for Pyrolysis of 1-Phenyl Tetradecane

Carbon Number of Side-Chain	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene
C ₁	3.2	—	7.3	—	12.5	—	14.8	—	14.4	—
C ₂	2.4	0.5	4.1	1.4	2.2	4.6	1.3	6.0	0.2	8.8
C ₃	0.2	0.2	0.3	0.4	1.0	0.3	1.3	0.2	1.3	—
C ₄	0.2	0.1	0.6	0.2	1.2	0.1	1.1	0.0	0.7	—
C ₅	0.1	0.3	0.2	0.4	0.9	0.2	0.8	0.1	0.5	—
C ₆	0.1	0.3	0.3	0.4	0.5	0.1	0.4	0.1	0.2	—
C ₇	0.1	0.3	0.2	0.4	0.3	0.1	0.2	0.1	0.2	0.1
C ₈	0.1	0.2	0.2	0.3	0.3	0.1	0.2	0.1	0.2	0.1
C ₉	0.1	0.2	0.2	0.3	0.2	0.1	0.2	0.1	0.1	—
C ₁₀	0.1	0.2	0.2	0.3	0.2	0.1	0.1	0.1	0.1	—
C ₁₁	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	—
C ₁₂	0.1	0.2	0.1	0.2	0.1	0.1	0.1	—	—	—
C ₁₃	0.2	—	0.2	0.1	0.1	—	0.1	—	—	—

Table A3a — Yield of n-alkanes and 1-alkanes from Pyrolysis of 2-n-Pentadecyl Pyridine

Carbon Number	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	n-al-kane	1-al-kene								
C ₅	0.2	0.5	0.7	0.9	1.1	1.2	2.1	1.2	1.6	0.7
C ₆	0.3	0.8	0.6	1.5	1.2	1.8	1.6	1.7	2.3	1.0
C ₇	0.3	0.6	1.2	1.1	1.1	1.3	1.6	1.2	1.7	0.3
C ₈	0.5	0.5	0.9	0.9	0.9	1.0	0.7	0.8	0.4	0.4
C ₉	1.2	0.3	0.5	0.5	0.9	0.9	0.2	0.6	0.1	0.4
C ₁₀	0.1	0.2	1.0	0.8	0.9	1.0	1.0	0.5	0.7	0.2
C ₁₁	0.2	0.7	0.6	0.7	0.6	0.9	0.5	0.3	0.4	0.1
C ₁₂	0.2	0.4	0.8	0.4	0.7	0.4	0.5	0.1	0.3	0.1
C ₁₃	1.5	0.4	3.1	0.3	2.7	0.4	1.5	0.1	0.7	—
C ₁₄	0.7	3.4	1.1	2.0	0.8	2.1	0.4	0.4	0.2	0.1

Table A3b — Yield of Substituted Alkanes and Alkenes from Pyrolysis of 2-n-Pentadecyl Pyridine

Carbon Number of Side-Chain	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene
C ₁	3.0	—	6.2	—	9.1	—	10.0	—	11.7	—
C ₂	0.5	0.5	0.9	1.8	2.6	—	3.9	—	4.4	—
C ₃	0.5	—	0.6	—	0.6	—	0.9	—	1.0	—
C ₄	0.2	—	1.0	—	0.9	—	0.9	—	0.7	—
C ₅	0.2	0.2	0.7	0.1	0.8	—	0.7	—	0.2	—
C ₆	0.2	0.3	0.5	0.1	0.5	—	0.8	—	0.2	—
C ₇	0.1	0.2	0.4	0.2	0.4	—	0.3	—	0.1	—
C ₈	0.2	0.2	0.2	0.4	—	—	0.2	—	0.2	—
C ₉	0.3	0.5	0.4	0.4	—	—	0.1	—	0.1	—
C ₁₀	0.2	0.2	0.4	0.2	0.2	—	0.1	—	—	—
C ₁₁	0.2	0.2	0.5	0.1	0.2	—	0.1	—	—	—
C ₁₂	0.2	0.2	0.4	0.1	0.2	0.1	0.1	—	—	—
C ₁₃	0.1	0.2	0.2	0.1	0.1	0.1	—	—	—	—
C ₁₄	0.4	—	0.4	0.1	0.2	—	—	—	—	—

Table A4a — Yield of n-alkanes and 1-alkenes from Pyrolysis of 2-Methyl Octadecane

Carbon Number	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	n-alkane	1-alkene	n-alkane	1-alkene	n-alkane	1-alkene	n-alkane	1-alkene	n-alkane	1-alkene
C ₅	—	0.6	0.5	0.5	1.8	1.2	2.9	1.2	2.2	1.4
C ₆	—	—	0.2	0.9	1.5	2.0	1.9	1.5	1.2	1.5
C ₇	—	—	0.2	0.7	0.7	1.4	2.0	1.1	1.2	1.2
C ₈	0.2	0.1	0.1	0.5	1.1	1.1	1.3	0.8	0.8	0.5
C ₉	—	—	0.1	0.5	0.5	1.0	0.9	0.5	0.4	0.5
C ₁₀	—	—	0.1	0.5	0.9	1.0	0.7	0.4	0.2	0.5
C ₁₁	—	0.1	0.1	0.4	0.3	0.9	0.6	0.3	0.2	0.3
C ₁₂	—	0.1	0.1	0.4	0.3	0.7	0.5	0.2	0.1	0.2
C ₁₃	—	0.2	0.1	0.4	0.2	0.6	0.3	0.1	0.1	0.2
C ₁₄	—	0.2	0.1	0.4	0.2	0.5	0.2	0.1	—	0.1
C ₁₅	0.1	0.1	0.4	0.3	0.8	0.4	0.7	0.1	0.3	—
C ₁₆	0.4	0.5	0.7	1.1	0.6	1.4	0.3	0.2	0.2	0.2
C ₁₇	—	—	0.1	0.3	0.1	0.1	—	0.1	—	—

Table A4b — Yield of Branched Alkanes and Alkenes from Pyrolysis of 2-Methyl Octadecane

Carbon Chain Length	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene
C ₅	—	—	0.1	0.2	0.3	0.6	1.1	0.6	0.8	0.7
C ₆	—	—	0.1	0.2	0.1	0.4	0.1	1.1	0.3	0.7
C ₇	—	—	—	0.3	0.2	0.6	0.5	0.9	0.4	0.7
C ₈	—	—	—	0.3	0.1	0.6	0.4	0.4	0.2	0.3
C ₉	—	—	—	0.3	0.2	0.6	0.4	0.2	—	0.2
C ₁₀	—	—	—	0.3	0.2	0.5	0.3	0.2	—	0.2
C ₁₁	—	—	0.1	0.3	0.1	0.5	0.3	0.1	—	0.2
C ₁₂	—	—	0.1	0.3	0.1	0.5	0.2	0.1	—	0.1
C ₁₃	—	—	0.1	0.3	0.2	0.4	0.2	0.1	—	—
C ₁₄	0.4	—	0.1	0.3	0.2	0.4	0.2	0.1	—	—
C ₁₅	0.1	—	0.1	0.3	0.2	0.4	0.2	—	—	—
C ₁₆	0.1	0.1	0.2	0.3	0.2	0.4	0.1	—	—	—
C ₁₇	0.3	—	0.3	0.1	0.2	0.1	—	—	—	—

Table A5a — Yield of n-Alkanes and 1-alkenes from Pyrolysis of n-Tridecyl Cyclohexane

Carbon Number	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	n-al-kane	1-al-kene								
C ₅	—	—	0.4	0.5	1.0	1.5	2.3	1.6	2.7	1.1
C ₆	—	—	0.5	1.3	0.7	2.2	1.6	2.1	2.0	1.1
C ₇	—	—	1.1	1.0	1.7	1.7	1.5	2.2	0.9	2.1
C ₈	—	—	0.4	1.0	0.4	1.2	0.9	1.2	0.9	1.3
C ₉	—	—	0.3	1.0	0.3	1.1	0.8	0.8	0.9	0.3
C ₁₀	—	—	0.3	1.0	0.3	1.0	0.6	0.6	0.6	0.2
C ₁₁	—	—	0.3	0.8	0.6	0.6	0.5	0.4	0.4	—
C ₁₂	0.1	—	1.1	0.7	0.6	0.5	1.0	0.3	0.7	—
C ₁₃	—	0.1	0.5	1.4	0.5	1.2	0.4	0.4	0.3	0.1

Table A5b — Yield of Substituted Alkanes and Alkenes from Pyrolysis of n-Tridecyl Cyclohexane

Carbon Number of Side-Chain	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene	al-kane	al-kene
C ₁	—	—	—	—	1.3	0.7	2.2	1.6	2.6	1.9
C ₂	—	0.5	0.9	—	0.6	0.9	1.2	0.8	1.4	0.3
C ₃	—	—	0.3	0.8	0.3	0.8	0.7	0.7	0.7	0.4
C ₄	—	—	0.3	0.7	0.2	0.6	0.5	0.3	0.4	—
C ₅	—	—	0.3	0.5	0.2	0.5	0.4	0.2	0.3	—
C ₆	—	—	0.4	0.6	0.2	0.5	0.4	0.2	0.3	—
C ₇	—	—	0.4	0.4	0.2	0.5	0.3	0.2	0.2	—
C ₈	—	—	0.3	0.5	0.2	0.5	0.2	—	0.2	—
C ₉	—	—	0.3	0.4	0.2	0.4	0.2	—	0.1	—
C ₁₀	0.2	—	0.4	0.4	0.3	0.4	0.3	0.1	—	—
C ₁₁	0.1	—	0.1	0.3	—	0.4	—	0.1	—	—
C ₁₂	0.3	0.1	0.2	0.1	—	—	—	—	—	—

Table A6 — Yield of n-Alkane and 1-alkene from Pyrolysis of n-Hexadecane

Carbon Number	Yield (%)									
	15 min		30 min		60 min		120 min		180 min	
	n-al-kane	1-al-kene								
C ₅	0.1	0.2	0.5	1.0	2.0	2.4	3.4	2.6	9.6	5.0
C ₆	—	0.1	0.3	1.5	1.7	3.2	2.5	3.1	4.0	2.3
C ₇	0.1	0.2	0.3	1.2	1.4	2.4	1.9	2.3	2.6	1.1
C ₈	—	0.1	0.2	1.1	0.9	2.0	1.1	1.7	1.6	0.8
C ₉	—	0.2	0.2	1.0	0.9	1.7	1.0	1.4	1.4	0.4
C ₁₀	—	0.2	0.2	1.0	0.8	1.5	0.8	1.1	1.0	0.3
C ₁₁	—	0.2	0.2	1.0	0.7	1.2	0.7	0.9	0.7	0.3
C ₁₂	—	0.2	0.2	0.9	0.7	1.1	0.6	0.7	0.5	0.2
C ₁₃	—	0.2	0.2	0.8	0.7	0.9	0.6	0.5	0.4	0.1
C ₁₄	—	0.2	—	0.8	0.3	0.9	0.2	0.5	0.2	0.1
C ₁₅	—	—	—	0.2	0.2	0.3	0.1	0.1	0.1	—