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stability of these distillates is a reflection of the intensity of hydrogenation. In spite of this intense hydrogenation the octane numbers indicate that the gasolines are not of the paraffinic type but rather of the paraffinic-naphthenic type in conformity with the structure of the crudes from which the charging stocks were obtained.

A word might be said of the important function of hydrogenation in the removal of sulfur, oxygen, and nitrogen. These elements are removed as hydrogen sulfide, water, and ammonia, respectively. The removal of sulfur may be represented by diethyl sulfide:

 $\begin{array}{l} ({\rm C}_{2}{\rm H}_{\rm 5})_2 \; {\rm S}({\rm g}) \; + \; 2{\rm H}_2 \; = \; {\rm H}_2{\rm S} \; + \; 2{\rm C}_2{\rm H}_{\rm 5} \; ({\rm g}) \\ + \; 6800 \; + \; 0 \; = \; -7840 \; - \; 21,400 \; + \; (-\; \Delta F^\circ_{\rm 298}) \\ {\rm or} \; (-\; \Delta F^\circ_{\rm 298}) \; = \; 36,040 \end{array}$

Thus at 298° K. there is a large driving force for the conversion of alkyl sulfides to hydrogen sulfide. Data on the free energy of organic sulfur compounds at high temperature

are not complete. However, a similar driving force undoubtedly exists, inasmuch as results on all types of petroleum hydrogenation always indicate effective removal of sulfur.

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RECEIVED September, 1933.

Pyrolysis of Saturated Hydrocarbons

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The literature is reviewed with special attention

✓ INCE petroleum is composed chiefly of saturated hydrocarbons, the study of the behavior of saturated hydrocarbons under cracking conditions forms an appropriate starting point for unraveling the complex reactions taking place in the several types of cracking operations in use. For many years cracking or pyrolysis of petroleum has been practiced for the purpose of making illuminating gas, benzene, kerosene, and gasoline. It has come to be appreciated that many pyrolytic reactions are involved. The primary reaction has been shown to be a splitting of the saturated hydrocarbon molecules into smaller complementary paraffins and olefins, sometimes accompanied by hydrogen. These

to the primary decomposition reactions. Paraffin hydrocarbons decompose chiefly into simpler complementary olefins and paraffins. High decomposition temperatures favor the concomitant formation of complementary olefins and hydrogen, and in some cases more than two hydrocarbon product molecules are formed. Two reaction mechanisms in accord with these observations have been proposed. The primary decomposition of cycloparaffins has not been investigated extensively.

By surface catalysis the paraffins are dehydrogenated to the corresponding olefins or degraded to carbon, methane, and hydrogen. The cyclohexanes are converted into the corresponding aromatics: the other cycloparaffins enter various rearrangements.

primary products may be converted in turn by prolonged heating into smaller molecules, the olefins first formed may polymerize to large molecules, and, when very drastic heating is employed, only the heat-stable aromatic hydrocarbons survive. However, the initial decomposition into paraffins and olefins is common to all pyrolytic processes applied to saturated hydrocarbons. Recent investigators have attempted to select experimental conditions which permit the study of primary decomposition itself.

From the scientific standpoint the investigation of hydrocarbon decomposition has become a more attractive field for research in recent years, since methods of analysis for hydrocarbon mixtures have been greatly improved, particularly by the development of precise laboratory methods for fractional distillation.

In the decomposition of saturated hydrocarbons by the agency of heat, the complexity of the situation is somewhat alleviated by the absence of polymerizing tendency and also by the endothermic nature of the reactions, which minimizes the possibility of thermal chains. Moreover, activation by

heat is less intense than by such means as electric discharge or radioactive disintegration. The presence of but two atomic species, carbon and hydrogen, and the new knowledge of the nature of the valence bonds and characteristic vibration frequencies of hydrocarbon molecules impart an added fundamental significance to work in this field.

DECOMPOSITION OF PARAFFINS

Because of the analytical difficulties, only the lower paraffins have as yet been studied for the purpose of determining the exact decomposition reactions. Decomposition takes place homogeneously in silica, Pyrex glass, and copper vessels.1

Temperatures of 500° to 700° C. and convenient pressures in the neighborhood of atmospheric usually have been employed (8, 20, 28)² If the heating is interrupted when a few per cent of decomposition has taken place, secondary decomposition is minimized.

The pyrolysis of methane has interested many investigators but because of its dissimilarity to the other paraffins will not be discussed here (8, 20, 24, 28, 43A)² Ethane decomposes into equivalent amounts of ethylene and hydrogen. Propane undergoes an analogous decomposition into propylene and hydrogen, but an equal amount decomposes by fracture of the carbon-carbon bond to produce equivalent amounts of the complementary ethylene and methane. Isobutane yields isobutylene and hydrogen, together with propylene and methane. The other paraffins studied decompose to only a small extent by the dehydrogenation

¹ Travers and Hockin (44A) report that the decomposition of ethane in a silica tube may be accelerated by hydrogen atoms resulting from inward diffusion of oxygen.

² The literature in this field is voluminous, specific reference is not made to all pertinent earlier work.

⁽⁹⁾ Ibid., p. 93.

route, fracture of the carbon-carbon bonds predominating. N-butane dehydrogenates to a limited extent to form all three of the isomeric normal butenes—namely, 1-butene and the *cis*- and *trans*- forms of 2-butene. For the greater part, however, the carbon chain breaks at the middle to yield ethylene plus ethane, and at the terminal position to yield propylene plus methane. In the same way isopentane yields by fracture at any position, 2-butene plus methane, isobutylene plus methane, propylene (or propane) plus ethane (or ethylene). 2, 3-Dimethylbutane yields trimethylethylene plus methane, and propylene plus propane. 2,2-Dimethylpropane yields isobutylene plus methane.

That a paraffin may decompose by fracture of the carbon chain to produce a smaller olefin and a complementary paraffin was recognized by Thorpe and Young (44) and others (8), and the more recent investigations (4, 11, 16, 21, 36, 37) have shown that any of the carbon-carbon bonds may break, and that virtually equivalent amounts of the two complementary molecules are formed in most cases. Hague and Wheeler (16) state that "the primary decomposition can be represented by a series of equations indicating the rupture of the chain at any position, with the production of an olefin and the complementary lower paraffin, or, at the limit, hydrogen." As will be seen, this rule is not selfsufficient. It does, however, represent satisfactorily the chief mode of decomposition. Such a decomposition is endothermic and absorbs about 20,000 calories per mole decomposed. Thermodynamic calculation shows that decomposition at moderate pressures should be nearly complete.

The following reactions represent the decomposition of isopentane which proceeds substantially according to rule; primary, secondary, and tertiary carbon atoms are all present, and any of the carbon-carbon bonds may break:

$$\begin{array}{c} CH_{s} \\ CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \longrightarrow CH_{3}CH=CHCH_{3} + CH_{4} \\ CH_{3} \\ CH_{3}CH:CH_{2}CH_{3} \longrightarrow CH_{3}CH=CH_{2} + CH_{1}CH_{3} \\ CH_{3}CH_{2}CH_{2}CH_{3} + CH_{2}=CH_{2} \\ CH_{3}CH_{2}CHCH_{2}:CH_{3} \longrightarrow CH_{3}C=CH_{2} + CH_{4} \\ \end{array}$$

The primary decomposition of the higher paraffins has been studied in a few cases, but analytical difficulties have stood in the way of obtaining exact interpretations. Sachanen and Tilicheyev (41, 42) have decomposed diïsoamyl (2,7-dimethyloctane) (425° C., 83 atmospheres, 63 minutes, 60 per cent decomposed) in an autoclave and analyzed the products by fractional distillation. Evidence of scission at all carbon-carbon bonds was obtained, and the products could be adequately accounted for by assuming that a paraffin and complementary olefin were formed. A little hydrogen was formed, however. Paraffin wax ($C_{24}H_{50}$ to $C_{26}H_{54}$) decomposed in the same way with less hydrogen formation. The products arising from scission at the center of the chain were somewhat the most abundant in both cases.

Most of the paraffins decompose to vield olefins capable of existing in isomeric forms, and it has sometimes been assumed that immediate rearrangement is to be expected. In a number of cases it has been shown that rearrangement does not take place, at least when the extent of decomposition is limited and the pressure low. N-hexane (9), decomposed in a silica tube to the extent of 17 per cent at 575° C. and 0.10 atmosphere pressure, yielded, among other products, 1-pentene and 1-butene and very little of the isomers, the double bond remaining at the point of rupture. N-pentane under similar conditions yielded 1-butene. Isopentane yielded 2-butene and isobutylene but not a mixture of the butenes in equilibrium proportions (10). Both the cis- and trans- forms of 2-butene were found in approximately the equilibrium ratio. In this case isomerization may have occurred. Hurd (19) has observed isomerization of 1pentene, 1-butene, and other simple olefins in an empty silica tube, but the conditions were more drastic.

In attempting to visualize how the decomposition takes place, a chief difficulty has been the transfer of a hydrogen atom from the carbon atom one removed from the point of fracture to the other fragment formed. Dissociation into alkyl radicals, one of which takes a hydrogen atom from the other, has been suggested (20). It has been thought that a prohibitively high activation energy may be required to effect dissociation into free alkyl radicals. To avoid this difficulty, Burk (3) has suggested that the one radical may transfer its allegiance to the hydrogen atom of the other radical by a semi-ionization process. Kassel (23) has suggested that the decomposition may proceed through the formation of paraffin and alkylidene, the alkylidene then rearranging to olefin.

Recent experiments have brought to light certain cases not covered by the rule as stated. Gault and Hessel (13) observed that apparently two complementary olefin molecules and one hydrogen molecule resulted from the primary cracking of hexadecane, and Frey and Hepp (9) observed that, in the decomposition of several isomeric pentanes and hexanes, a part of the expected complementary paraffin (ex-

		ISOPENTANE			-N-PENTANE-		<u> </u>		
Expt.	1	2	3	1	2	3	4	5	6
Temp., °C. Pressure, mm. Time, sec. % decomposed k ₁	$^{398}_{560}_{14400}_{1.8}_{1.3 \times 10^{-6}}$	$575 \\ 77 \\ 12.2 \\ 7.6 \\ 0.0065$	570 76 16.1 8.25 0.0054^{a}	396 510 14800 1.3 9 × 10-7	560 ^b 74 27 7.8	560 77 16.6 4.9 0.0031 ^c	425b 140 5400 10.3 2×10^{-5}	575 77 4.5 5.5 0.013	575 76 11.1 17.0 0.017
Analysis of products H ₂ CH ₄ C ₂ H ₄ C ₃ H ₅ C ₃ H ₅ C ₄ H ₆ (CH ₃) ₂ C:CH ₂ C ₄ H ₆ (CH ₃) ₂ C:CH ₂ C ₄ H ₅ CH:CH ₂ CH ₄ CH:CHCH ₂ CH ₄ CH:CHCH ₃ C ₄ H ₁₀ C ₅ H ₁₀ C ₅ H ₁₂ C ₆ H ₁₄ Heavier	$\begin{array}{c} \text{a, mole } \%: \\ 1 \\ 33 \\ 5 \\ 5.5 \\ 7.5 \\ 4 \\ \end{array} \right\} 10.5 \\ 11.5 \\ \\ 32.5 \\ 10.5 \\ 11.5 \\ \\ \\ \\ \\ \\ \\ \\ \end{array}$	$ \begin{array}{c} 10 \\ 31.5 \\ 10.5 \\ 4 \\ 13.5 \\ 14.5 \\ 14.5 \\ 14.5 \\ 14.5 \\ 14.5 \\ 14.5 \\ 11.5 \\$	$\begin{array}{c} 7.5 \\ 31 \\ 11 \\ 5.5 \\ 14.5 \\ 1 \\ 15 \\ \\ 28.0 \\ 2.5 \\ 1.5 \\ \\ 2.5 \\ 1.5 \\ \\ \\ \end{array}$	$\begin{array}{c} 2 \\ 19 \\ 7 \\ 24 \\ 5 \\ 22 \\ 3 \\ 25.0 \\ 0 \\ 9 \\ 2 \\ 11.0 \\ 2 \\ 2 \\ 12 \\ \dots \\ 12 \\ \dots \\ \dots \\ \dots \\ \dots \end{array}$	$\begin{array}{c} 10 \\ 19 \\ 19 \\ 14.5 \\ 2^2 \\ 1 \\ 0.5 \\ 11.5 \\ 11.5 \\ 12.5 \\ 0.5 \\ 2 \\ \cdots \\ \cdots \\ \cdots \\ \cdots \\ \cdots \\ \cdots \end{array}$	$ \begin{array}{c} 10 \\ 18 \\ 20 \\ 15.5 \\ 20 \\ 1 \\ 20 \\ 1 \\ 21 \\ 0.5 \\ 11.5 \\ 11.5 \\ 13.0 \\ 1 \\ 2.5 \\ \dots \\ $	$\begin{array}{c} 0.5 \\ 15 \\ 18.5 \\ 13.5 \\ 19.5 \\ 6.5 \\ 26.0 \\ \cdots \\ 9 \\ 0.5 \\ 10.0 \\ 10.0 \\ 10.5 \\ \cdots \\ 6 \\ \cdots \\ 6 \\ \cdots \end{array}$	$\begin{array}{c} 3.5\\ 22.5\\ 28.0\\ 11\\ 18.5\\ 0.5\\ 9\\ 9.5\\ 0.5\\ 4.0\\ 2.5\\ \dots\\ 2.5\\ \dots\\ \end{array}$	$\begin{array}{c} 2 & 5 \\ 23 & 5 \\ 25 & 5 \\ 11 \\ 20 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ $
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
		0.0000 1.77							

TABLE I. DECOMPOSITION PRODUCTS OF ISOPENTANE, N-PENTANE, AND N-HEXANE

^a k₁ corrected to 575° C. is equal to 0.0066. b Temperature was erratic. c k₁ corrected to 575° C. is equal to 0.0057.

cepting methane) appeared instead as the corresponding olefin and hydrogen, even though such a decomposition is the more endothermic by about 30,000 calories per mole. The decomposition reaction is apparently not simple. Moreover, Gault and Hessel (13) have obtained evidence of the formation of more than two hydrocarbon product molecules in the decomposition of hexadecane. Frey and Hepp (9) have found (Table I) N-pentane and N-hexane, unlike the other lower paraffins studied, to yield about 2.5 hydrocarbon molecules per molecule decomposed at 575° C. Both these observations indicate that reactive intermediate molecules may be formed in the primary decomposition. Direct evidence of the formation of reactive intermediates in the decomposition of paraffins has been obtained by Rice (39) who passed propane, butane, and other organic materials through a highly heated tube at high velocity and low pressure. The effluent gases exhibited the property of removing metallic mirrors. The gases were allowed to impinge on metallic mercury. Mercury dialkyls were formed, and methyl and ethyl radicals identified.

Rice has proposed a theory (38) for the decomposition of paraffins based on the formation of free alkyl radicals which leads naturally to the formation of more than two hydrocarbon product molecules from N-pentane and N-hexane, and just two from the other lower paraffins studied. A few molecules are assumed to dissociate into free alkyl radicals, each of which may then initiate a reaction chain by extracting a hydrogen atom from another paraffin molecule which thus becomes in turn an alkyl radical and may then decompose by fracture of the carbon chain at that point which will allow of the formation of a molecule of olefin and a simpler complementary alkyl radical without migration of hydrogen. The simpler alkyl radical in turn extracts hydrogen from a paraffin molecule, and so the chain continues. Free alkyl radicals may lose as well as gain a hydrogen atom and survive as either the corresponding paraffin or olefin. It is possible in the case of N-pentane and N-hexane to represent the formation of a radical capable of undergoing two consecutive decompositions, splitting off on each occasion a molecule of olefin. The decomposition of N-pentane (38) is represented as follows:

The net result may be represented as follows:

$$\begin{array}{ccc} C_5H_{12} \longrightarrow C_2H_4 + C_2H_4 + CH_4 \\ C_5H_{12} \longrightarrow C_3H_6 + C_2H_6 \ (\text{or} \ C_2H_4 + H_2) \\ C_5H_{12} \longrightarrow C_4H_8 + CH_4 \end{array}$$

That alkyl radicals actually undergo such decomposition readily is supported by experiments (9A) in which di-N-

butylmercury and di-sec-butylmercury decomposed to yield apparently ethylene plus ethyl and propylene plus methyl, respectively, since N-hexane was formed in the former case and isopentane in the latter, presumably by union of the radicals so produced with the accompanying butyl radicals. Experiments also have been conducted³ which indicate that endothermic reaction chains may be initiated by free alkyl radicals. N-butane containing one per cent and less of dimethylmercury was heated to 525° C. for a time sufficient to decompose most of the dimethylmercury but too short to decompose butane. Twenty equivalents and more of butane decomposed into the usual products, however, and an additional quantity of methane was present equivalent to the methyl groups in the mercury alkyl decomposed.

Kassel (25) has recently proposed a theory, based on fundamental valence considerations, which accounts for the formation of more than two product molecules without the formation of free alkyl radicals. In the case of N-butane, for example, two hydrogen atoms at opposite ends of the carbon chain are assumed to come into proximity and unite with each other to form a free hydrogen molecule. The carbon chain breaks in the middle to form two ethylene molecules. N-pentane similarly may yield methane and two ethylene molecules, and higher paraffins decompose similarly.

The experimental evidence at present available cannot be considered to furnish conclusive proof for any theory. The decomposition is, in any event, complex, and additional quantitative critical data are desirable.

ROLE OF TIME, TEMPERATURE, AND PRESSURE VARIABLES

Apart from the question of reaction mechanism, investigations dealing with the effect of time, temperature, and pressure bring to light some characteristics of the decomposition reactions which have not yet been made the subject of extensive theoretical treatment.

TIME (EXTENT OF DECOMPOSITION). In order to obtain primary products, the extent of decomposition must be limited. The ordinary paraffins and olefins resulting from the primary decomposition are seldom less stable than the original paraffin, and little secondary decomposition of the ordinary kind ensues when less than 10 per cent of primary decomposition is permitted. The changes taking place too rapidly to be ascribed to such ordinary secondary decomposition have all been considered a part of the primary decomposition. Elevated pressures must be avoided to minimize polymerization. Accordingly, most investigators of primary decomposition have employed low extents of conversion, pressure of one atmosphere or less, and convenient temperatures of 500° to 750° C.

Schneider and Frolich (43) and Marek and co-workers (29, 30, 33) have attempted to examine closely the primary changes by conducting a series of pyrolysis experiments at otherwise constant conditions, but permitting variation in exterb of decomposition. The yields of the several products were extrapolated to zero extent of decomposition. With less than 10 per cent decomposed at 650° C., N-butane (33) yielded ethylene and hydrogen in place of a part of the ethane, in addition to the usual products. Other simple paraffins show this effect (9), and it has been observed in the case of N-butane to be very marked at high temperatures (5). This type of decomposition may be represented as follows:

$$C_{3}H_{6} + CH_{4}$$
 (1)
 $C_{2}H_{4} + C_{2}H_{4} + H_{2}$ (2)

$$\begin{array}{c} C_{2}\Pi_{4} + C_{2}\Pi_{5} \\ C_{4}H_{8} + H_{2} \\ \end{array}$$

³ Investigation in progress.

Reaction 2 predominates at high temperatures and 3 at low temperatures (400° C.); 1 and 4 take place at all temperatures. Reaction according to Equation 2 cannot be ascribed to ordinary secondary decomposition but is a part of the complex primary decomposition, or an accelerated dehydrogenation taking place in the presence of a concurrent primary decomposition. 2,3-Dimethylbutane (\mathcal{G}) at 575° decomposes in part in the same way:

 $C_6H_{14} \longrightarrow C_3H_6 + C_3H_6 + H_2$

Scission products of propane are not formed to any extent. The formation of either a paraffin or a corresponding olefin is accommodated by the Rice theory if we assume that an alkyl radical formed in the course of primary decomposition may either gain a hydrogen atom at a low temperature or lose a hydrogen atom at a high temperature, and survive either as a paraffin or the corresponding olefin.

The anomalous decomposition of N-pentane and N-hexane to form more than two hydrocarbon product molecules likewise is not due to ordinary secondary decomposition as it is marked when the extent of decomposition is small.

Schneider and Frolich (43) have recovered small amounts of butane from the products of decomposition of propane and have suggested the bimolecular reaction:

$$2C_8H_6 \longrightarrow C_2H_6 + C_4H_{10}$$

TEMPERATURE. Decomposition rates have been determined for gas oil (14, 15, 26), 2,3dimethylbutane, N-hexane (9), N-heptane (37A)and all the lower paraffins (2, 9, 21, 29, 30, 33-37). A wide temperature range has been covered, but

precise data are few in the range below 500° C. A correlation of rate data by Geniesse and Reuter (15) is shown in Figure 1. (For subsequent work see also citations 9, 26, 30, 33, 37A). The decomposition rates at a given temperature increase regularly with molecular weight, and among the lower paraffins at least structure has a minor effect. The rate constant at 575° C. increases from k_1 second = 0.0002 for ethane to k_1 second = 0.08 for gas oil. The strength of the valence bonds in the paraffin molecule would be expected to vary but slightly with molecular weight. Pease (36) accounts for the difference in decomposition rates by suggesting that the frequency with which a molecule finds itself active will be greater the more complex the molecule, since the total energy available for concentration on some particular degree of freedom increases with the number of atoms in the molecule. Burk (3) has considered theoretically the mechanism of energy transfer within the molecule and has calculated the change in reaction rate to be expected for normal paraffins with change in molecular weight. Heats of activation of 73,200 to 46,500 calories per mole have been calculated from rate data (9, 15, 26, 37, 37A) for paraffins ranging from ethane to gas oil (15) containing substantial amounts of paraffins in the neighborhood of C17H36. The average corresponds to a rate increase of threefold per 25° C. at 550°, increasing to fivefold at 400°. For a homogeneous reaction of this kind a true threshold temperature below which decomposition does not take place would not be expected. Norris and Thompson (34, 35) have determined the decomposition rates, in a Pyrex glass bulb, of pentanes, butanes, and N-hexane at temperatures of 340° to 500° C. There was evidence of the existence of significant temperatures below



FIGURE 1. VARIATION OF REACTION VELOCITY CONSTANT WITH TEMPERATURE

which the scission of the paraffin molecule was confined to a single one of the several carbon-carbon bonds. Frey and Hepp (\mathcal{P}) , on the contrary, have reported scission of all carbon-carbon bonds in isopentane and N-pentane below the significant temperature marking the upper limit for single-bond scission.

While the outstanding effect of temperature is its influence on reaction velocity, it also affects somewhat the composition of the primary reaction products. It has been pointed out that any of the carbon-carbon bonds may break. While experimental data comprise only propane, the butanes and pentanes, and two hexanes (9, 29, 30, 33), it has been shown that the relative amounts of scission at the various bonds are affected only a little by temperature over the rather wide range studied (395° to 675° C.). Adequate analytical data are not available for the higher paraffins, but it is probably true that scission takes place at any of the carbon-carbon bonds, and increasing temperature accelerates them all nearly, but not quite, equally.

The temperature does, however, affect the olefin-paraffin ratio in the products (Equation 2). It has been pointed out that product paraffins higher than methane appear partly in the form of the corresponding olefins and hydrogen, and that this effect, negligible at 400° C., may predominate at 575° and higher. While thermodynamic considerations must be applied to cracking reactions with caution, the dehydrogenation equilibria for reaction of the type,

$\mathrm{C_nH_{2n}}_{+2} \leftrightarrows \mathrm{C_nH_{2n}} + \mathrm{H_2}$

appear to be reflected in the composition of the products of primary decomposition. At 400° C. and 760 mm. pressure, ethane, propane, and N-butane are dissociated under equilibrium conditions to the extent of 1.2, 4.5, and 8.5 per cent, respectively (10), and the dissociation is approximately doubled by a 50 °C. temperature increase. The homogeneous decomposition of paraffins does not produce paraffins and their corresponding olefins in equilibrium ratios, but ethane to ethylene, propane to propylene, and butane to butylene ratios tend to parallel the equilibrium values. Analyses of the products obtained by decomposing several paraffins at 575 °C. and 0.10 atmosphere are shown in Table I. The products containing over two carbon atoms per molecule are almost wholly olefinic. A similar result will no doubt be obtained in the case of somewhat higher paraffins for which, however, adequate data are not now available.

The tendency for N-pentane and N-hexane and presumably many higher paraffins to break into more than two hydrocarbon product molecules is greatly increased by increase in temperature (Table I), and this effect together with the dehydrogenation effect discussed (Equation 2) tend to produce both a greater number of product molecules and a greater proportion of olefins and hydrogen at high temperatures than at low temperatures. N-hexane, for example (Table I), produces 2.5 hydrocarbon molecules at 575° C. and 2.1 at 425°. While the Rice mechanism cannot be applied with complete confidence to higher paraffins, there is evidence that something of this kind takes place. Hexadecane (12) (550° C., 1 atmosphere, about 40 per cent of decomposition) produced approximately equal weights of gaseous and liquid products. At a low temperature relatively less gas would be expected by analogy with the results of other investigators.

The high ratio of gas to gasoline obtained in the vaporphase cracking of gas oil is due in part to the low extent of polymerization taking place at the low pressures used, but the course taken by the primary decomposition at a high temperature must also be partly responsible for high gas yield as well as for the low content of paraffins in the gasoline.

PRESSURE. The primary decomposition of paraffins is a homogeneous first order reaction, and pressure variations within a wide range have little effect on the reaction velocity. Pease (37) has shown that propane and butane undergo little change in decomposition rate as pressure is decreased somewhat below atmospheric, but at a pressure of 2 mm. of mercury the falling off in rate characteristic of homogeneous unimolecular reactions becomes marked. At pressures higher than atmospheric little change in cracking velocity is evident up to 50 atmospheres at least. The decomposition of Midcontinent gas oil at atmospheric pressure (15) and at 50 atmospheres pressure (26) has been shown to proceed at nearly the same rate at any temperature over a rather wide range. Little information is at hand concerning cracking at extremely high pressures. Hugel and Artichevitch (17) decomposed hexadecane at 500 atmospheres and at 400° and 470° C., and believed the high pressure lowered the decomposition rate. This observation has also been made in connection with the cracking of oil at a high pressure (25A). Other effects due to extreme pressure can be expected to complicate the problem, notably secondary synthetic reactions which would follow the primary cracking closely and run concurrently. Products both heavier and lighter than hexadecane were found in approximately equal amount in the 400° experiment. The thermodynamic calculations of Parks (35A) are interesting in this connection.

While little experimentation has been carried out under pressure in which strictly primary reactions were studied, much research has been conducted dealing with hydrocarbon mixtures and under conditions related to practical cracking (41, 46, 47). McKee and Szayna (32) have studied the cracking of individual heptanes and octanes by following the changes in critical temperature. Hugel and Szayna (18) have studied the pyrolysis of N-octane and hexadecane under high pressures and obtained evidence of isomerization of paraffins.

Apart from pressure itself, the effect of liquid state as contrasted with the gaseous state on decomposition rate has received attention, and conflicting views have been expressed (27, 31, 41). That decomposition rates differ little at the same temperature is indicated by the experiments of Keith, Ward, and Rubin dealing with gas oil (26). In a part of the temperature-pressure range covered, 426° to 482° C. (800° to 900° F.), and 51 atmospheres (750 pounds per square inch) the oil was in the liquid state, but the rates differed little from those obtained at atmospheric pressure (15) by Geniesse and Reuter.

DECOMPOSITION OF CYCLOPARAFFINS

Interest in the pyrolysis of cycloparaffins is partly due to the bearing of the Baeyer strain theory on their stability in relation to ring size. The abundance of cycloparaffins in petroleum also lends interest to the subject. A complete review of the literature has been published (γ) .

In most of the pyrolytic studies dealing with cycloparaffins, catalysts have been used, and, while the specificity of catalysts stands in the way of determining comparative ring stability by their use, several interesting characteristic effects have been observed. Cyclopropane, methyl-, ethyl-, and 1,1-dimethylcyclopropane, and methylcyclobutane have been decomposed at 300° to 400° C. in the presence of alumina (6, 22, 40) and yielded mainly the isomeric olefins through rupture of the ring. Cycloheptane has been converted into methylcyclohexane (48) and cycloöctane into methylcycloheptane and bicycloöctane by dehydrogenating catalysts (49). Cyclohexane and other cycloparaffins containing the hexamethylene ring are dehydrogenated reversibly in a characteristic manner by nickel or palladium to the corresponding aromatic hydrocarbons (50). The decomposition of paraffins is also catalyzed by many substances (8), but little information is available in regard to the reactions taking place. Nickel, iron, and a number of other metals cause formation of carbon, methane, and hydrogen. Chromium oxide (10) in an active form, and activated charcoal (8) bring about dehydrogenation to the corresponding olefins.

A few of the cycloparaffins have been pyrolyzed without a catalyst. At 550° C., rearrangement of cyclopropane into propylene was nearly complete in 20 minutes (1). Small amounts of scission products were formed. Cyclohexane, methylcyclohexane, and other cycloparaffins yield a variety of aliphatic scission products (8) and often aromatics. They differ from the paraffins of similar molecular weight in their greater stability to heat. This property complicates the study of primary reactions, since primary products may be decomposed even though little of the cycloparaffin is converted. Virtually none of the cycloparaffins has been pyrolyzed under such conditions that the primary reactions are clearly evident.

In Table II are shown analyses of the products resulting from the decomposition of cyclopentane and cyclohexane in an empty silica tube following a procedure described elsewhere (\mathcal{P}) . Ordinary secondary decomposition was no doubt appreciable. The products obtained from cyclopentane may be approximately accounted for by the following:

$$C_{6}H_{10} \xrightarrow{T} C_{5}H_{6} + C_{2}H_{4}$$
$$\xrightarrow{T} C_{5}H_{8} + H_{2} \xrightarrow{T} C_{5}H_{6} + 2H_{2}$$

The products from cyclohexane (Table II) cannot be accounted for in a simple way. An experiment in which only 1.6 per cent decomposition was permitted gave a similar

product analysis except for a much higher proportion of pentadienes. Pease (37A) has observed an induction period in the pyrolysis of cyclohexane and obtained evidence of isomerization, probably to methylcyclopentane. Benzene formation was not marked. Consequently the formation of aromatics from the corresponding cycloparaffins cannot in general be said to take place primarily by simple dehydrogenation of the ring when catalysts are absent. Cyclohexanes containing long paraffinic side chains can be expected to decompose chiefly by scission in the side chains.

TABLE 1	II. I	DECOMPOSITION	OF (Cycloparaffins
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	Cyclopentane	Cyclohexane
Temp., ° C.	574	622
Pressure, mm. Hg	76	68
Reaction time, min.	10	0.7
% decomposed	22.1	24.4
Sample decomposed, grams	2.5^{a}	10.3
k_1 , sec.	0.0005	0.0066
k_1 calcd. for 575° C., sec.	0.0005	0.0008
Analysis of products, mole %:		
\mathbf{H}_2	7.8	8.1
CH_4	1.5	3.3
C_2H_4	6.5	8.4
C_2H_6	0.7	3.7
$C_{3}H_{6}$	8.9	5.6
C ₃ H ₈	0.6	0.2
$C_{4}H_{6}$	{o}	$\{4, 1, \dots, n\}$
$C_{4}H_{8}$	(°),	(5.0
$C_{\delta}H_{s}, C_{\delta}H_{10}$	D.40	1.64
		2.14
Cyclopentane	00.5	57 04
Cyclonexane		07.0*
Uighan budnaaanhana	9.16	0.4
nigher nyurocaroons	2.10	0.0
Total	100.0	100.0

^a The sample was small; a 12-gram sample (not reported) decomposed under slightly different conditions gave a very similar product analysis, however.
^b Cyclic olefins and diolefins, 2.7 per cent cyclopentadiene.
^c Distilling above cyclopentane.
^d Cyclic olefins and diolefins, 0.5 per cent cyclopentadiene.
^e No test was made for methylcyclopentane.

SECONDARY REACTIONS IN PYROLYSIS

The foregoing discussion has been confined to the primary reactions taking place in the pyrolysis of saturated hydrocarbons. In practical cracking operations secondary reactions play an important part (11A). Paraffins and olefins formed by primary decomposition may both be decomposed to smaller molecules by prolonging the exposure to a pyrolysis temperature. Olefins may also undergo rearrangement and polymerization. Cyclic hydrocarbons (cycloparaffins and aromatics) formed in the course of polymerization may survive prolonged heating because of their greater stability to heat.

In commercial oil cracking operations some gasoline is produced by primary decomposition reactions. As reaction is prolonged, not only does the quantity of gasoline increase but also the proportion of the lower boiling gasoline hydrocarbons and gaseous hydrocarbons increase as secondary splitting reactions take part. At the same time tar is produced by polymerization and the quantity is greater under high than low operating pressures. Aliphatic polymers are readily destroyed by prolonged heating, and the survival of synthesized cyclic molecules first becomes apparent in the higher boiling products of cracking, but later in the lower boiling products.

Temperature and pressure are important operating variables, and in practice the higher pressures are usually associated with the lower temperatures, and vice versa, by reason of plant design requirements. Further research can be expected to show more clearly that variation in temperature and pressure each produces characteristic individual effects.

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RECEIVED September 7, 1933.

The seeds sown by research have proved unusually productive during the past few lean years. S. K. COLBY