[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Thermal Cracking of Higher Paraffins

BY H. H. VOGE AND G. M. GOOD

The decomposition of paraffins with two to eight carbon atoms has been quite well explained as being predominantly a chain reaction involving free radicals. The radical theory accounts for the products,[1,2] the inhibition of cracking by nitric oxide[3,4] and olefins,[4] and the initiation of cracking by mercury dimethyl[5] and other materials that readily produce radicals.[6] In addition, alkyl radicals have been detected in hydrocarbon systems undergoing decomposition at reduced pressures.[2,7] The cracking of paraffins containing more than eight carbon atoms has not been adequately tested against the theory, yet such materials offer a more stringent test of predicted products of reaction. Although a few examples of the cracking of higher hydrocarbons are to be found in the literature, such as the fine early studies of Gault and Hessel[8] and Gault and Sigwalt,[9] they are not adequate for detailed comparison. The data given in the present paper enable comparisons to be made between predicted and observed products of cracking and also furnish rates of cracking that lead to a general equation for the cracking velocities of normal paraffins. The experiments were made in connection with a study of catalytic cracking,[10] and supplied data on *n*-dodecane, an isododecane, and *n*-hexadecane. The results are compared with those predicted by the radical chain theory and by the alternative theory of Burk.[11]

Experimental

All experiments were made in a system for flowing reactants. The equipment and procedure were essentially as described previously.[10a,12] The reactor tubes were of 18–8 chromium–nickel steel (A.I.S.I. type 302) of $^1/_2$, 1, or $1^1/_2$-inch iron pipe size. Temperature control in the center of the tube was within ±3° of the specified value. The reactor tubes were vertical, and were filled with clean, dense quartz chips of 6–14 mesh (inch) size to aid heat transfer and prevent laminar flow. In the run at elevated pressure, the system was initially pressured with nitrogen, and at the end of the experiment, the pressure was reduced to atmospheric before the commencement of the usual nitrogen flush.

Analysis of gases was by low temperature distillation followed by sulfuric-acid absorption for olefins or infrared spectrophotometry for isomeric olefins and paraffins. Liquid products were distilled in a column of 14 mm. i.d. and 76 cm. length, packed with $^3/_{16}$ inch diameter helices. The fractions were analyzed for olefins by bromine number (bromine in carbon tetrachloride method), and for aromatics by ultraviolet absorption, or in some cases by acid absorption corrected for olefins or by refractive dispersion.

Although the cracking experiments were made in "stainless steel" tubes, there was no evidence of catalysis by the tube walls, which were maintained in an oxidized condition by treatment with air at 500–600° in the regenerations following each run of two to ten hours' duration. In other experiments not reported here, it has been noted that when stainless steel tubes develop catalytic activity, usually at 550° or above, they do so quite suddenly, and produce large amounts of hydrogen and carbon. No such effects were observed in the present experiments. The non-catalytic properties of oxidized stainless steel tubes have also been mentioned by Marschner,[13] who showed that they gave the same results as Pyrex in the cracking of *n*-octane. Nevertheless, we are uncertain whether all the coke and hydrogen arose from uncatalyzed reactions, and have not attached significance to the quantities of these materials.

Results of Cracking *n*-Hexadecane.—The *n*-hexadecane (cetane) was from du Pont, with $n^{20}D$ 1.4346, d^{20}_4 0.7741, m.p. 17.0°, and b.p. 287.7° at 761.3 mm. Results from two cracking runs at atmospheric pressure, and one at a pressure of 21 atmospheres absolute, are shown in Table I, while Table II gives the products as moles from each 100 moles of hexadecane cracked. Conversions were computed from the amount of material in the range C_1 through C_{14}, together with hydrogen and coke. The C_{15} material was not included because the amount was not always determined; actually the C_{16} fraction was 0.9% of the charge in the run at 21 atmospheres, and should be less in the other runs at lower conversions. Material other than hexadecane in the products boiling above 273° was also quite small, as judged by the refractive index of that fraction from the run at 31.5% conversion, which was $n^{20}D$ 1.4360 (hexadecane feed 1.4346).

Reaction velocity constants were computed for a first order reaction, since the first order law, $kt = \ln 100/100 - C$, where C is the percentage conversion, is known to hold approximately for the thermal decomposition of paraffins at a given pressure. The residence time, t, is not directly measurable in a flow system, and therefore the proper equation for a flow system, first given by Benton,[14] was used. This is

$$kG/V = N \ln\ (100/100 - C) - (N - 1)\ C/100$$

where k is the rate constant in sec.$^{-1}$, G is the void hot volume of the reactor in cc., V is the influx gaseous flow rate in cc. per sec. at reaction temperature and pressure, N is the moles of product per mole of hexadecane cracked, and C is the percentage conversion. The void volume of the quartz chips was 45% of the gross volume. In computing the volume G, correction was made for the temperature profile, by weighting small sections of the tube in accordance with relative reaction velocities at the observed temperatures, to get an equivalent volume at 500°. This was done by assuming an activation energy of 60 kcal. per mole. Actually, about 95% of the equivalent volume was between 495 and 503°. After k

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(1) W. G. Appleby, W. H. Avery and W. K. Meerbott, THIS JOURNAL, **69**, 2279 (1947), and references cited therein.

(2) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935.

(3) L. A. K. Staveley and C. N. Hinshelwood, *Trans. Faraday Soc.*, **35**, 845 (1939), and earlier work by the same authors.

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(5) F. E. Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

(6) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946.

(7) G. C. Eltenton, *J. Chem. Phys.*, **15**, 455 (1947).

(8) H. Gault and F. A. Hessel, *Ann. Chim.*, [10] **2**, 319 (1924).

(9) H. Gault and R. Sigwalt, *Annales de l'Office National des Combustibles Liquides*, **2**, 309, 543 (1927).

(10) (a) B. S. Greensfelder and H. H. Voge, *Ind. Eng. Chem.*, **37**, 514 (1945); (b) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **37**, 1168 (1945).

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(12) (a) H. H. Voge, G. M. Good and B. S. Greensfelder, *Ind. Eng. Chem.*, **38**, 1033 (1946); (b) H. J. Henriques, *ibid.*, **39**, 1564 (1947).

(13) R. F. Marschner, *Ind. Eng. Chem.*, **30**, 554 (1938).

(14) A. F. Benton, THIS JOURNAL, **53**, 2984 (1931).

TABLE I

THERMAL CRACKING OF *n*-HEXADECANE AT 500°

Conditions			
Pressure, atm. abs.	1	1	21
LHSV[a,b]	0.046	0.10	3.0
Flow, moles/l./hr.[b]	0.156	0.337	10.1
Duration, hr.	10.5	4.5	2.0
Material balance, %w			
Gas through C_4	17.9	11.9	13.8
C_5-C_9 liq. (to 152°)	14.2	9.8	18.0
C_{10}-C_{14} liq. (to 255°)	9.0	9.4	14.3
C_{15} liq. (to 273°)	57.6	69.3	0.9
C_{16} and higher			51.0
Coke	1.3	0.7	0.9
Loss	0.0	−1.1	1.1
Computed data, no loss basis			
Conversion, % (through C_{14})	42.4	31.5	47.5
Rate constant, *k*, sec.$^{-1}$	0.0026	0.0032	..
Residence time, sec.	211	118	84
Olefin contents of liquid fractions, %w			
C_5	94	99	63
42–99°	91	90[c]	68
99–125°	..	..	67
152–174°	..	..	70
Aromatic contents of liquid fractions, %w			
42–99°	2	1	2
99–125°	4	3	6
125–152°	..	..	12
Above 255°	..	..	0

[a] Liquid hourly space velocity. [b] LHSV and flow rate based on void space (45% of gross volume) at 495–503°. [c] 42–74° fraction.

had been computed from the above equation, the residence time, *t*, was obtained from the usual first order law. Since the first order law probably does not hold exactly, *k* and *t* are approximations. The values of *k* in the two experiments at atmospheric pressure, 0.0026 and 0.0032 sec.$^{-1}$ agree moderately well, and are also in approximate agreement with an earlier rough value of 0.004[10a] at 4% conversion. The experiment at 21 atmospheres led to a higher value of 0.0078, but since this has not been checked, it is not now taken as indicating that cracking rate increases with pressure. The primary interest in the experiment at 21 atmospheres lies in the nature of the products.

The products from thermal cracking of hexadecane, listed in Table II, cover the full range from methane upward, but methane, ethylene, ethane and propylene are especially prominent at atmospheric pressure. The elevated pressure of 21 atmospheres causes an increased saturation of the fractions, and a general shift of products toward higher molecular weights. Analyses of a few of the liquid fractions, included in Table I, indicate that olefin contents were very high for the atmospheric pressure runs. In the run at 21 atmospheres, olefin contents were lower and aromatic and paraffin contents were higher.

TABLE II

PRODUCTS FROM THERMAL CRACKING OF *n*-HEXADECANE

Pressure, atm. abs.	1	1	21
Conversion, %	42.4	31.5	47.5
Products, moles per 100 moles of hexadecane converted			
H_2	16.5	16.7	17.4
CH_4	50.9	53.0	23.3
C_2H_4	84.0	76.9	14.9
C_2H_6	56.6	52.6	38.0
C_3H_6	59.0	47.4	27.1
C_3H_8	16.5	13.0	36.5
C_4H_6	1.7	1.6	0.9
i-C_4H_8	1.6	1.6	0.8
n-C_4H_8	18.5	16.6	18.3
i-C_4H_{10}	0.6	0.8	0.8
n-C_4H_{10}	2.7	2.0	13.0
t-C_5H_{10}	2.8	2.8	2.2
s-C_5H_{10}	12.0	5.7	12.1
i-C_5H_{12}	0.4	0.1	1.0
n-C_5H_{12}	0.6		7.1
C_6 (42–74°)	26.5	24.3	26.3
C_7 (74–99°)	14.5	16.2	18.6
C_8 (99–125°)	12.7	13.4	12.2
C_9 (125–152°)	10.5	10.1	13.2
C_{10} (152–174°)	5.7	10.9	11.0
C_{11} (174–196°)	5.2	9.3	9.2
C_{12} (196–217°)	7.5	7.3	8.2
C_{13} (217–238°)	7.2	7.7	6.2
C_{14} (238–255°)	3.1	4.9	7.0
Total	417.3	394.9	325.3

Radical Theory of Cracking

Rice and Rice[2] noted that the products from the cracking of *n*-hexadecane as observed by Gault and co-workers[8,9] were in general agreement with the predictions of the radical chain theory. The present data permit a much more detailed comparison, and show that while the simple theory of Rice and Rice[2] overemphasizes certain products, the improved theory of Kossiakoff and Rice[15] gives better agreement.

According to the radical chain theory, small alkyl radicals accumulate to a steady state concentration. These radicals remove hydrogen atoms from paraffin molecules, leaving a large radical which will decompose rapidly in definite ways, ultimately regenerating a small radical which continues the chain. Reasonable values for the parameters determining products were set forth by Kossiakoff and Rice,[15] and almost the same values have been adopted here. The rate of removal of secondary hydrogen is taken to be greater than that of primary hydrogen by a factor of 3.66 at 500° (exp $(2000/RT)$). The total rate of removal of each type is proportional to the number of such atoms multiplied by this factor. The relative rate of removal of a tertiary hydrogen at 500° is 13.4 (exp $(4000/RT)$).

Radicals formed by removal of hydrogen atoms rupture at a carbon–carbon bond that is removed by one carbon atom from the hydrogen-deficient carbon (that is, at a beta bond). There are good reasons why the rupture occurs only at the beta bonds.[16] No carbon–hydrogen bonds are made or broken when rupture occurs, and the products are always an olefin and a smaller radical. When alternative beta bonds are available, the relative rates of cracking are determined by the resonance

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(15) A. Kossiakoff and F. O. Rice, THIS JOURNAL, **65**, 590 (1943).

(16) C. E. H. Bawn, *Trans. Faraday Soc.*, **34**, 598 (1938); F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

stabilizations of the radicals that crack off. For simplicity in view of lack of accurate knowledge, the relative rates of cracking have been taken as follows, corresponding to exp(1700/RT), and powers thereof.

Radical cracked off	Relative rate
Methyl	1
Ethyl and higher primary	3
Secondary	9
Tertiary	27

The theory described so far may be called the simple chain theory. It is compared with experimental results in Table III. The amount of ethylene predicted is much too great. Most of this ethylene arises from the breakdown of large primary alkyl radicals, which, according to the simple theory, continue to split off ethylene until they are reduced to the methyl or ethyl radicals that appear in the final products as methane or ethane. An amplification of the theory introduced by Kossiakoff and Rice[15] overcomes this difficulty by assuming that the large radicals, although too short-lived to be converted to paraffins, are sufficiently long-lived to undergo isomerization prior to rupture. In the present work it is assumed as by Kossiakoff and Rice, that the radical position can only shift by a coiling mechanism to a carbon atom separated by three or more carbon atoms from the original position. Therefore, C_3, C_4 and C_5 radicals do not isomerize; among the hexyl radicals only the 1- and 2-forms are taken to be interconvertible; for the heptyl, the 1-, 2- and 3-; and for the higher radicals, all possible isomers obtainable by a shift of a hydrogen atom. Branched chain radicals are not formed from straight chains by these isomerizations. In computing the equilibrium among the radicals immediately prior to their cracking, the secondary are estimated to be 4,000 cal. per mole more stable than the primary, and the tertiary another 4,000 cal. per mole more stable than the secondary. Thus the relative weights at 500° are 1, 13.4 and 47.7 for primary, secondary and tertiary, and of course these weights have to be multiplied by the appropriate statistical factor.[15]

TABLE III

EXPERIMENTAL AND THEORETICAL PRODUCTS FROM HEXADECANE

	Moles per 100 moles cracked		
	Experimental	Theoretical	
Product		Simple	With isom.
CH_4	53.0	50.7	61.2
C_2H_4	76.9	338.7	99.9
C_2H_6	52.6	49.4	38.8
C_3H_6	47.4	13.5	50.3
C_3H_8	13.0	0	0
C_4H_6	1.6	0	0
i-C_4H_8	1.6	0	0
n-C_4H_8	16.6	10.1	27.2
C_4H_{10}	2.8	0	0
C_5H_{10}	8.5	6.8	14.9
C_5H_{12}	0.1	0	0
C_6	24.3	6.8	16.5
C_7	16.2	6.8	14.0
C_8	13.4	6.8	12.3
C_9	10.1	6.8	10.9
C_{10}	10.9	6.8	9.9
C_{11}	9.3	6.8	8.9
C_{12}	7.3	6.8	7.8
C_{13}	7.7	6.8	7.1
C_{14}	4.9	6.8	7.0
C_{15}	...	3.4	3.5
Total hydrocarbon	378.2	533.8	390.2
H_2	16.7	0	0

In computing the predicted products from the cracking of n-hexadecane by the amplified radical theory of Kossiakoff and Rice, every radical formed in the process of decomposition was taken to isomerize to equilibrium before cracking further, except for the C_7 and smaller, as noted above. The restriction on the degree of isomerization of the smaller radicals is rather arbitrary, since it is conceivable that isomerization may occur by a simple shift of a hydrogen atom rather than by a coiling mechanism. In the case of n-hexadecane, however, this restriction makes little difference because of the relatively small number of isomerizations excluded. Table III shows that the products predicted by the chain theory with radical isomerization agree well with those observed in cracking at atmospheric pressure. Comparison has been made with the run of 31.5% conversion, but the other run agrees about as well. It would be more desirable to compare experimental cracking at very low conversions, since the theory is for the initial cracking and does not take into account secondary decomposition of initial products. However, secondary cracking reactions will change the theoretical values of Table III less than 15% at conversions below 30% according to some unpublished calculations made with the simple radical theory by Drs. R. S. Rasmussen and D. P. Stevenson of these laboratories.

The agreement obtained using radical isomerization is suggestive, but is not a full proof of this step for alternative, more complex, explanations of the products are conceivable.

A graphical comparison of theoretical and experimental results from hexadecane is given in Fig. 1, in which products are grouped by carbon number. As noted above, agreement is quite good. The more detailed data of Table III show a few discrepancies. For example, the theoretical amount of ethylene is somewhat high, even with radical isomerization. Likewise some propane is obtained, indicating that the theoretical assumption that all propyl radicals decompose is not correct. Other deviations are minor, such as the failure to predict traces of butadiene and isobutylene, present in the experimental products in amounts scarcely greater than the error of analysis. One of the most important predictions of the theory is the absence of paraffins above ethane.

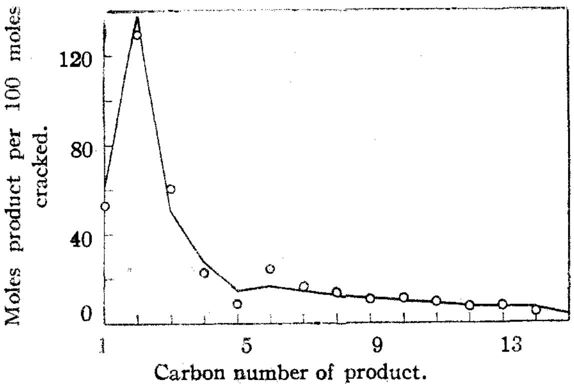

Fig. 1.—Experimental and theoretical product distributions from hexadecane at 500°: circles, experimental, 31.5% conversion; line, theoretical, with radical isomerization.

With the exception of propane, this is well borne out. Very small amounts of paraffins are found in the C_4, C_5, and liquid fractions. Similar results have been observed for the thermal cracking of paraffin wax at low pressures and in the presence of steam diluent.[17] The wax consists primarily of normal paraffins, C_{20} to C_{28}, and liquid products from cracking are 90% olefinic, or more.

No attempt was made to compute the products from cracking at elevated pressure. Certain qualitative aspects are in good agreement with the principles of the radical chain theory, such as the presence of paraffins above ethane, and the higher average molecular weight. At 21 atmospheres it is thought that some of the higher radicals are converted to paraffins before they can decompose. This also accounts for the lesser amount of ethylene.

Cracking of Dodecanes

Products from the thermal cracking of an isododecane were given in a previous paper.[10a] The isododecane was made by hydrogenation of the trimer of isobutene obtained in the polymerization with cold sulfuric acid, and there are valid reasons for believing that the predominant structure present was 2,2,4,6,6-pentamethylheptane. Calculations of the products theoretically expected from this structure were made under the same assumptions employed above. The experimental and theoretical products are compared in Table IV. The agreement is a little better without radical isomerization, but there is not a large difference between the two cases as there was with *n*-hexadecane. The correspondence of calculated and experimental products is considered fairly good. It is of interest that no C_2 is predicted and very little is found. Also, butane is predicted in the observed quantity, in contrast with normal paraffins where no paraffinic products above ethane are theoretically expected.

Experimental results from thermal cracking of *n*-dodecane at 550°, previously published,[10a] are in qualitative agreement with the results from *n*-hexadecane and with the amplified radical chain theory.

TABLE IV

EXPERIMENTAL AND THEORETICAL PRODUCTS FROM ISODODECANE

Experimental results from cracking at 500° and atmospheric pressure (ref. 10a), with 15.1% conversion

Product	Moles per 100 moles cracked Experimental	Theoretical Simple	With isom.
C_1	53	73	73
C_2	7	0	0
C_3	20	17	7
$i\text{-}C_4H_8$	86	57	43
$n\text{-}C_4H_8$	5	0	0
$i\text{-}C_4H_{10}$	25	27	27
$n\text{-}C_4H_{10}$		0	0
C_5	76	0	0
C_6		0	0
C_7		24	29
C_8		27	27
C_9		0	0
C_{10}		0	0
C_{11}		32	37
Total hydrocarbon	272	257	243
Hydrogen	24	0	0

Direct Fission Theory and Rates of Cracking

Before the development of the chain theory, Burk[11] suggested that cracking might occur by direct fission of a paraffin into a smaller paraffin and an olefin. He also proposed[11,18] a general equation for the rate of cracking of normal paraffins, namely, $k = (n - 1)v \exp(-E/RT)$, where k is the first order rate constant, n is the number of carbon atoms, and v and E are constants for the homologous series. It is now clear that the direct fission theory does not explain the products of cracking, for it predicts only two moles of product per mole cracked, and a mixture of olefins and paraffins for all carbon numbers two or more below that of the paraffin cracked (except, of course, for C_1). The rate equation was tested by Burk, Laskowski and Lankelma[18] with available data by computing values of E from the known values of the reaction rates, k, and a constant value of v. They obtained E's varying from 59 to 65 kcal. From the approximate constancy of E, they concluded that the data supported the equation and mechanism of Burk.

The rate constant obtained in this work for hexadecane has been combined with a few other values from the literature in another test of the above equation. The present test has been made by plotting values of $k/(n - 1)$ against n for a single temperature. According to the Burk equation for the rate of cracking, a horizontal line should result. Data for the plot are given in Table V, and Fig. 2 shows the result. It is seen

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[17] For example, A. J. van Peski, U. S. Patent 2,172,228 (1939).

[18] R. E. Burk, L. Laskowski, and H. P. Lankelma, THIS JOURNAL, 63, 3248 (1941).

that $k/(n - 1)$ increases in a regular fashion with increasing n. It is concluded that the equation is not a very good approximation. Instead, the following empirical relationship, taken from the straight line drawn in Fig. 2, may be written for the rate of cracking of normal paraffins at 500°

$$k\ (\text{sec.}^{-1}) = (n - 1)(1.57\,n - 3.9) \times 10^{-5}$$

and atmospheric pressure, for $4 \leq n \leq 16$. Actually the agreement of the experimental points with this line in Fig. 2 is better than can be expected, considering the variations in k normally met. It is not thought that the above empirical equation represents the true relationship for n-paraffins, but simply that it is a useful approximation. It should also be stressed that expression of the rates by means of first order constants in itself is an approximation, because the most careful work shows first order rate constants usually decrease somewhat with increasing depths of cracking.

TABLE V

THERMAL CRACKING RATES FOR n-PARAFFINS, C_nH_{2n+2}

n	Ref.	First order rate const., sec.$^{-1}$ k at temp., °C.	 k at 500°	$k \times 10^5/$ $(n - 1)$
4	4	2.06×10^{-4}, 520	0.80×10^{-4}	2.7
4	19	1.32×10^{-4}, 513	0.66×10^{-4}	2.2
7	1	5.5×10^{-3}, 552	3.8×10^{-4}	6.3
8	13	3.9×10^{-3}, 538	6.0×10^{-4}	8.6
12	10a	1.8×10^{-2}, 550	16.8×10^{-4}	15.3
16	20	3.2×10^{-3}, 500	32×10^{-4}	21.3

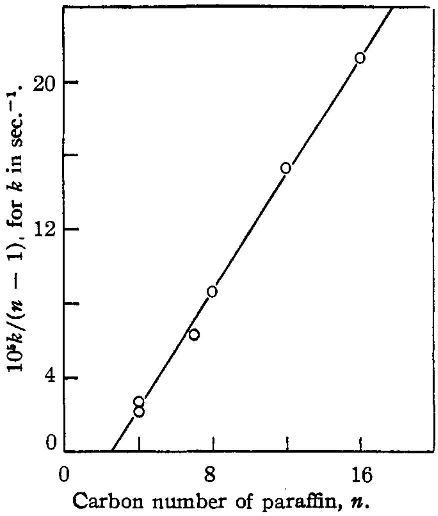

Fig. 2.—Variation of cracking rate constant with carbon number for n-paraffins at 500°.

The rate constants given in Table V are from experiments in which conversion lay between 10 and 32% (except for dodecane at 41%) and the pressure was atmospheric or very close to atmospheric. If rates at 500° were not given, they were converted from the nearest available temperature, using the activation energy given by the same author, or 60 kcal. if no other was stated. Although this procedure is not as satisfactory as would be measurements on a number of homologs in one apparatus at one temperature, it is considered sufficiently accurate for the test presented here.

Acknowledgment.—Dr. B. S. Greensfelder gave valuable encouragement. Mrs. S. S. Tornbom assisted in the performance of the experiments.

Summary

The thermal cracking of n-hexadecane was observed in a system for flowing reactants at 500° and pressures of one and 21 atmospheres absolute. Detailed analyses of the products are given, and those at one atmosphere are shown to be in good agreement with the predictions of the Rice radical chain theory as amplified by Kossiakoff and Rice. Earlier data for the products from an isododecane are also shown to agree with the theory. Rates of cracking for homologous normal paraffins are approximately represented by first order rate constants, which do not fit an equation proposed by Burk, but lead to the empirical relationship $k\ (\text{sec.}^{-1}) = (n - 1)\ (1.57\,n - 3.9) \times 10^{-5}$ for rates at 500°.

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(19) E. W. R. Steacie and I. E. Puddington, *Can. J. Research* **B16**, 176 (1938).

(20) This work.