The Catalytic Cracking of Aliphatic Hydrocarbons*

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The thermal decomposition of long-chain aliphatic hydrocarbons is characterized by non-selective chain scission which is undesirable from a utilitarian viewpoint; but little systematic work has been done to develop catalysts which would induce a selective chain splitting. A review of the field[1] led to the conclusion that difficultly reducible refractory oxides were the best potential catalysts for carbon–carbon bond scission. In the present work the effect of an activated silica–alumina mass on the reactions of n-butenes, n-pentenes, n-octenes, cetene, n-octane and cetane was studied under conditions which allowed comparisons between (1) the catalyzed and the uncatalyzed reactions; (2) the cracking of paraffins and olefins of the same chain length and (3) homologs in both the paraffin and the olefin series.

Reactions of n-Butenes.—A mixture of n-butenes has been reported to isomerize to isobutene in the presence of a catalyst consisting of phosphoric acid on various supports.[2,3] Frost and co-workers[2] found that the reversible isomerization of butenes-1 and -2 to isobutene followed the equilibrium equation

$$\log K_p = \frac{304}{T} \; 0.528 \pm 0.020$$

At 300° the equilibrium mixture contained equal amounts of straight chain and branched chain butenes.

In our experiments the n-butenes were passed over the catalyst at temperatures varying from 385 to 600°; the results are summarized in Table I.

It is apparent that under the conditions employed considerable polymerization to higher-boiling materials and decomposition to lighter gases accompanies the isomerization to isobutene. The yield of liquid products reached a maximum of about 25% at 450° (at flow rates of 200–230 volumes of gas per volume of catalyst per hour) and then declined; the yield of light gases in-creased steadily with rise of temperature, but sharply decreased with rise of flow rate.

At space velocity 200–230, the isomerization was not sensitive to temperature change between 450 and 600°; the C_4 fraction of the product contained 24.1 ± 1.5% of isobutene. The total isobutene yield was raised, however, by increasing the space velocity at 600°, since the side reactions were cut down while the isobutene content of the C_4 product was unchanged. The fact that a 5.7-fold increase of space velocity produced no change in the isobutene content points to the attainment of a pseudo-equilibrium; that true equilibrium was not reached is indicated by the isobutene/n-butene ratio, which never exceeded 0.40, although according to the equation of Frost and co-workers[2] the equilibrium ratio ranges from 1.0 at 300° to 0.66 at 600°.

Reactions of n-Pentenes.—The catalytic isomerization study was extended to the next higher homologs, n-pentenes. Although the thermal isomerization of both pentene-1 and -2 into isopentenes has been reported,[4] the work was not corroborated in a later publication by the same author,[5] and no reliable evidence of such isomerization, either thermal or catalytic, has been published[6]; the inter-isomerization of pentene-1 and -2, however, has been definitely established.[4,5]

n-Pentenes prepared by the catalytic dehydration of n-amyl alcohol were passed over the present catalyst at 400° with the results shown in Table II.

Distillation of the C_5 fraction after it had been hydrogenated over a nickel catalyst at 100° showed that it contained 82% of isopentane and 18% of n-pentane. The conversion of n-pentenes to methylbutenes, therefore, was 53%[7]; at the same time about 8% of gas and 17% of material boiling above pentenes were formed. Since the molar ratio of C_4 to C_6 hydrocarbons recovered was about 1.2, it seems likely that the major portion of these hydrocarbons was formed by the decomposition of pentene dimer.

(1) Egloff and Bloch, *Proc. Second World Petroleum Congr., Paris, France*, **2** (II), 461 (1937).

(2) Frost, Rudkovskiĭ and Serebryakova, *Compt. rend. acad. sci. U. R. S. S.* (N. S.), **4**, 373 (1936); Serebryakova and Frost, *J. Gen. Chem. (U. S. S. R.)*, **7**, 122 (1937).

(3) N. V. Bataafsche Petroleum Maatschappij, French Patent 823,545, Jan. 21, 1938.

(4) Hurd, *Ind. Eng. Chem.*, **26**, 51 (1934).

(5) Hurd, Goodyear and Goldsby, THIS JOURNAL, **58**, 235 (1936).

(6) Norris and Reuter, THIS JOURNAL, **49**, 2626 (1927).

(7) Allowing for 12.5% of isopentenes present in the charging stock; see Experimental Part.

TABLE I
ISOMERIZATION OF n-BUTENES

Furnace temp., °C.	385	400	450	500	550	600	600
Duration, hr.	0.75	2	2	2	2	2	0.5
Space velocity (gas), av.	525	200	230	230	225	205	1160
Wt. { H.-b. prods.	14	20.2	24.3	20.5	14.4	8.9	12.7
% { Gas	86	79.8	75.7	79.5	85.6	91.1	87.3
of { Light gas (C_3 and lower)	2.8	7.2	13.1	17.1	21.0	31.4	15.7
charge { Isobutene	8.0	11.6	14.1	15.9	15.0	14.2	17.1
C_4 fraction, % isobutene	9.6	16.1	22.6	25.6	23.3	23.8	23.8
Ratio isobutene/n-butenes	0.11	0.20	0.33	0.40	0.37	0.38	0.34
H_2	0.0	0.5	0.0	0.0	4.9	17.5	1.3
CH_4	0.0	0.3	0.0	0.0	8.7	18.6	3.1
C_2H_4	0.0	0.0	0.0	0.1	2.2	2.8	0.4
C_2H_6	0.0	0.0	0.0	1.1	2.1	3.4	1.6
Gas C_3H_6	3.5	10.4	17.9	22.6	18.7	14.0	17.3
anal., C_3H_8	0.7	1.0	3.9	3.3	1.7	2.5	1.8
vol. i-C_4H_8	9.2	14.1	17.7	18.7	14.4	9.8	17.8
% n-C_4H_8		69.4	53.0	46.5	38.9		52.9
	85.6					25.7	
C_4H_6		0.6	0.2	0.4	0.3		0.9
C_4H_{10}	1.0	3.7	7.3	7.4	8.2	5.6	3.0

TABLE II
CATALYTIC DECOMPOSITION OF n-PENTANES[a]

Furnace temp., °C.		400
Duration, hr.		0.75
Space velocity		3.2
Pentenes charged, g.		150
Prod- { Gas, b. p. <15°		7.6
ucts, { C_5, b. p. 15–45°		71.7
wt. { C_6, b. p. 45–72°		7.7
% { C_7–C_9, b. p. 72–150°		3.8
of { C_{10} and bottoms, b. p. >150°		5.1
charge { Unaccounted		4.1
Gas { H_2		4
anal- { C_2H_4		3
ysis, { C_3H_6		5
vol. { i-C_4H_8		34
% { n-C_4H_8		28
{ C_nH_{2n+2} (index = 2.21)		26

[a] Contains 12.5% or less of iso-pentenes.

TABLE III
CATALYTIC CRACKING OF n-OCTENES

	375	385	400
Furnace temp., °C.	375	385	400
Duration, hr.	2.45	0.5	0.5
Space velocity	4.1	4.2	4.1
n-Octenes charged, g.	720	151	148
Liquid recovered, g.	646	125	117
Liquid product, { C_5 + C_6 + C_7, b. p. 10–95°	10.9	8.3	
wt. % of { i-C_8, b. p. 95–121.5°	58.2	60.5	
charge { n-C_8, b. p. >121.5°	20.6	14.7	
Weight % of charge	8.5	14.4[a]	17.5[a]
Volume, liters (N. T. P.)	27.0	9.6	11.3
Molecular weight	50.6	51.1	51.3
Gaseous product — Anal., vol. % { H_2	0.1	0.0	0.0
{ CH_4	0.8	0.0	0.0
{ C_3H_6	35.7	27.5	32.4
{ C_3H_8	2.1	1.7	1.9
{ i-C_4H_8	30.6	32.5	27.8
{ n-C_4H_8	22.4	32.3	28.9
{ C_4H_{10}	8.3	6.0	9.0
Unaccounted, wt. % of charge	1.8	2.1	3.4

[a] These gasifications correspond to an initial period of high catalytic activity.

Reactions of n-Octenes.—n-Octenes (prepared by the catalytic dehydration of octanol-2) not only isomerized when passed over the catalyst but also decomposed. The 20% cracking at 375° is in striking contrast to the 0.4% reaction of n-octenes obtained thermally at 364–369° by Hugel and Szayna[8] and the 7% obtained by them at 438–444°. The results of the catalytic cracking at 375, 385 and 400° are summarized in Table III.

The composition of the gases produced catalytically is in sharp contrast to that obtained by Hugel and Szayna in thermal cracking. At 438–444°, the gas formed in the latter process contained over 90% of paraffins and hydrogen; the

(8) Hugel and Szayna, *Ann. combustibles liquides*, **1**, 781 (1926).

gas obtained by catalytic cracking contained approximately 90% of propene and butenes, and only traces of materials lighter than the three-carbon hydrocarbons. The composition of the catalytically produced gas is unusual also for the fact that approximately equal quantities of normal and isobutene were present; this was especially true of the runs at 385 and 400°. This isobutene could be formed in at least three ways: (1) direct cracking of the n-octenes to give two straight-chain butenes followed by the isomerization of the n-butenes; (2) direct cracking of the n-octenes into two straight-chain C_4 radicals which are isomerized before rearranging to the

olefin, and (3) the isomerization of the n-octenes to iso-octenes followed by cracking of the iso-octenes to yield isobutene.

Since this catalyst was also studied with n-butenes under similar conditions without producing equal amounts of iso- and n-butenes, hypothesis (1) seems unlikely. We have no direct evidence for or against hypothesis (2). Since iso-octenes were isolated there is little doubt that hypothesis (3) is entirely possible. Thus, although we are not able to exclude hypothesis (2), we are inclined to favor hypothesis (3).
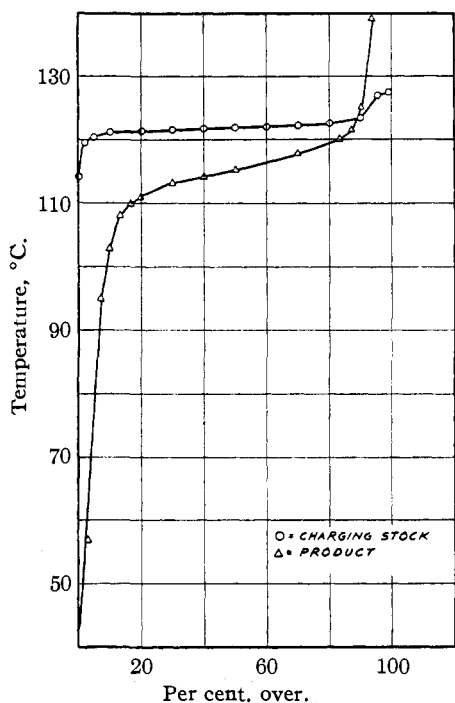

Fig. 1.—Catalytic decomposition of octenes -1 and -2 at 385°.

A study of the distillation curve of the liquid product obtained at 385° (Fig. 1) confirms the isomerization of the octenes; approximately 80% of the octene fraction consisted of iso-octenes boiling lower than the original but boiling above any C_7 olefins. In the 375° run, approximately 75% of the octene fraction consisted of these isoöctenes, as shown in Table III. The catalyst employed in this work was a more effective isomerizing agent than zinc chloride or phosphoric acid on pumice, which, according to Petrov and Cheltsova,[9] converted a mixture of octenes-1 and -2 to a maximum of 45–47% of isoöctenes, under com-

(9) Petrov and Cheltsova, *Compt. rend. acad. sci. U. R. S. S.*, **15**, 79 (1937).

parable temperature conditions, but with much longer periods of contact.

To determine the constituents of the isoöctene fraction obtained at 375°, all of the product boiling below 121.5° was hydrogenated in the presence of a nickel catalyst at 100° and 100 kg./sq. cm. pressure, and the saturated product distilled on a 50 bubble-plate column of the Bruun type.[10] The distillation curve is shown in Fig. 2. From this curve and refractive indices of several of the fractions, the following hydrocarbons are suggested as likely constituents.[11]
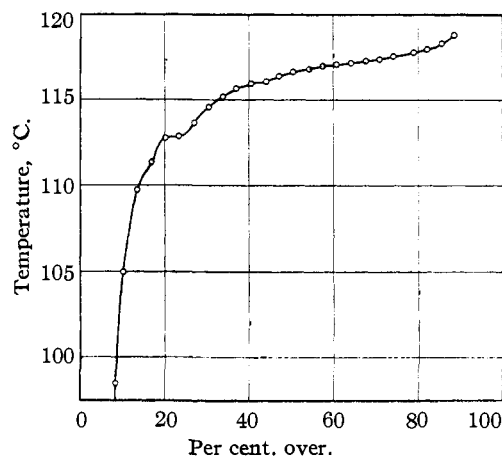

Fig. 2.—Hydrogenated isoöctenes formed from octenes-1 and -2 at 375°.

2,3,4-Trimethylpentane (b. p. 113.8°) corresponding to the first plateau (113.8–113.9°), is the only octane boiling between 111.5 and 114.6° except 2-methyl-3-ethylpentane (b. p. 114°) which is another possibility but is considered less likely.

2-Methylheptane (b. p. 117.2°) corresponds to the second plateau (117.0–117.1 corr.).

4-Methylheptane (b. p. 118.0°) and/or 3,4-dimethylhexane (b. p. 117.9°). The fraction boiling at 117.0–118.0° (corr.) had a refractive index (n^{20}D 1.3987) which indicated that it was probably a mixture of 2-methylheptane (n^{20}D 1.3936) and one or both of the above (n^{20}D 1.4035 and 1.4044, respectively). It seems less likely to contain 3-ethylhexane (b. p. 118.6°, n^{20}D 1.4014) and unlikely to be 3-methyl-3-ethylpentane (b. p. 118.4°, n^{20}D 1.4081).

3-Methylheptane (b. p. 119.0°, n^{20}D 1.3982). The fraction boiling at 118.0–118.8° (corr.) had a

(10) Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).

(11) Grosse and Egloff, "Physical Constants of Paraffin Hydrocarbons," published by Universal Oil Products Co., Chicago, Ill., 1938.

refractive index n^{20}D 1.3982, lower than that of the preceding fraction, and the fraction boiling at 118.8–119.8° (corr.) had an index n^{20}D 1.3987. Since 3-methylheptane is the only octane boiling in this range with a refractive index below 1.4, considerable amounts of this hydrocarbon must have been present.

The over-all picture indicates that the catalyst effects extensive isomerization of n-octenes to methylheptenes, dimethylhexenes, and trimethylpentenes, probably by the migration both of alkyl groups and of the double bond. The isoöctenes then crack under the influence of the catalyst, principally to n- and isobutenes and to propene and pentenes.

The octene product was hydrogenated and fractionated into an isoöctane cut boiling at 106–119° (corr.). The A. S. T. M. octane number of this cut was 48.5; that of n-octane (obtained by hydrogenating the n-octenes used in these experiments) in the same engine was −20. This is additional proof that the carbon skeleton of the octene has been changed since, in general, the higher octane number of a given molecular weight

Fig. 3.—Distillation of hydrogenated gasoline from catalytic cracking of cetane.

paraffin is usually associated with the most highly branched isomer.

Cetene Cracking.—From a study of the thermal reactions of cetene at 350 to 725°, Gault and his co-workers[12] concluded that at the lower temperatures olefinic products predominated, while at higher temperatures alicyclic and aromatic hydrocarbons were formed in increasing amounts. The maximum production of olefinic gases (66–68% of the gaseous product) occurred at 575 to 700°, while initial cracking of the cetene began at 450 to 550°, depending on the contact time. Hugel and Goldthorpe[13] found that metallic catalysts lowered the temperature at which reaction began.

With the catalyst used in the present work cetene showed incipient reaction at 300° with a liquid space velocity of four. The gasification under these conditions was only 0.07%, but 8% of the product (neglecting a small amount of residue) boiled over a 6° range immediately below the original boiling range (at reduced pressure). At 350° about 5.5% of the charge was cracked to gasoline and gas; but of the hexadecenes recovered, almost 50% boiled within a 9° range just below that of the original cetene. This fraction was believed to consist of lower-boiling isohexadecenes, since there were no gaseous products such as would have accompanied the formation of 14- and 15-carbon molecules. In run B-331 this lower-boiling hexadecene fraction was catalytically cracked at 350° under the same conditions as were employed for the original cetene; three times as much cracking was effected. These results tend to confirm the tentative conclusions reached in the n-octene experiments, namely, that the cracking of normally liquid straight-chain olefins over the present catalyst is largely preceded by isomerization.

The data obtained in the cracking of cetene at 300° to 450° are summarized in Table IV.

It will be noted that the proportion of low-boiling hexadecenes in the C_{16} fraction increases with rising temperature, until practically no cetene is left in the hexadecene fraction of the 450° run.

In order to approximate the course of the reactions, the products were expressed as moles formed per 100 moles of cetene converted to
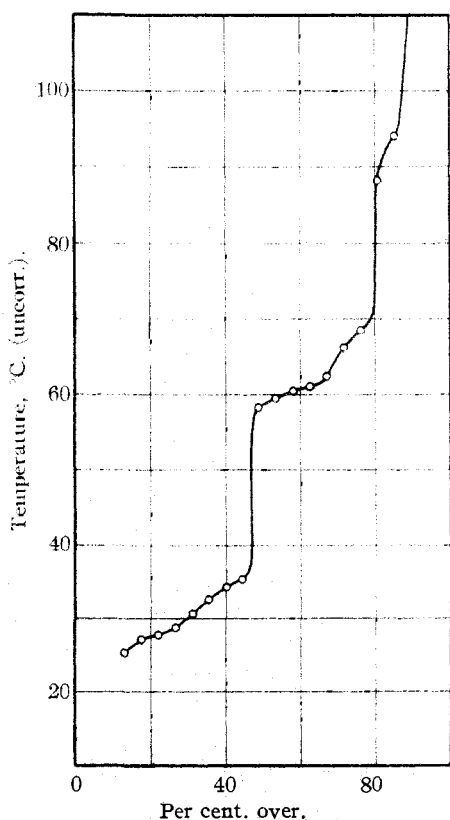
(12) Gault and Altchidjian, Compt. rend., **178**, 2092 (1924); Ann. chim., (10) **2**, 209 (1924); Gault, Hessel and Altchidjian, Compt. rend., **178**, 1562 (1924).

(13) Hugel and Goldthorpe, Ann. combustibles liquides, **3**, 613 (1928).

TABLE IV

CATALYTIC CRACKING OF CETENE

	300	350	350ᵃ	400	450
Furnace temp., °C.	300	350	350ᵃ	400	450
Duration, hr.	3.93	4.0	2.67	4.0	2.78
Space velocity	4.0	4.0	4.0	4.1	4.0
Cetene charged, g.	1230	1255	830	1270	885
Liquid products, wt. % of charge — Total	99	99.5	98.5	95	84
Gasoline, b. p. 10–200°	0.0	5.1	15.1	43.0	59.5
Octane number (A. S. T. M.)	...	...	..	77.8	80.6
Octane number after hydrogenation	...	...	..	34.1	51.6
Intermed. fr., 200° (750) to 125° (14 mm.)	0.0	0.6	1.1	5.8	8.0
Low-boiling hexadecenes	8.0	44.9	70.9	26.9	13.0
Cetene and bottoms	91.0	47.5	9.9	18.3	1.1
Gaseous product, Anal., vol. % — Weight % of charge	0.07	0.44	1.1	4.5	14.1
Molecular weight	49.2	51	51.5	51	51.2
H_2	0.0	0.0	1.5	0.0	0.0
CH_4	0.0	0.0	1.2	0.0	0.0
C_2H_4	20.3	0.7	0.0	3.9	0.0
C_2H_6		7.3	0.9	0.9	0.0
C_3H_6	3.5	12.2	18.1	25.8	32.8
C_3H_8	29.7	17.0	4.6	2.1	3.2
$i\text{-}C_4H_8$	5.6	14.6	29.5	28.6	27.4
$n\text{-}C_4H_8$		16.8	36.2	29.2	29.8
C_4H_{10}	41.0	31.4	8.0	9.4	6.9
Unaccounted, wt. % of charge (including distillation losses)	0.9	1.6	1.9	1.6	4.3

ᵃ Charge contained 90% of low-boiling hexadecenes, 10% of cetene.

lower-boiling products (other than hexadecenes). The results are shown in Table V.

TABLE V

PRODUCTS OF CETENE DECOMPOSITION

Furnace temp., °C.	350	350ᵃ	400	450
Decomposition, %	6.1	17.3	53.3	81.6
H_2	0.0	0.4	0.0	0.0
CH_4	0.0	0.3	0.0	0.0
C_2H_4	0.2	0.0	1.4	0.0
C_2H_6	2.0	0.2	0.3	0.0
C_3H_6	3.9	4.8	9.2	25.0
C_3H_8	5.4	1.2	0.8	2.4
$i\text{-}C_4H_8$	4.7	7.8	10.2	21
$n\text{-}C_4H_8$	5.4	9.6	10.4	23
C_4H_{10}	10.2	2.1	3.4	5.2
C_5	16ᵇ	18.8ᶜ	22.6	36
C_6	14.7	18.2	26.1	40
C_7	18.0	19.5	23.7	32
C_8	34.2	27.0	25.6	24
C_9	25.2	21.0	23.3	16
C_{10}	51.4	58.0		17.3
C_{11}			10.7	18
C_{12}			10.0	
C_{13}				6.2
C_{14}	11.6	6.7	13.0	0.0
C_{15}	0.0		0.0	0.0
Total	202.9	195.6	208.0	248.8

(Left margin label: Moles per 100 moles of cracked cetene)

ᵃ From low-boiling hexadecenes. ᵇ Of which only 10.2 were recovered, 5.8 assumed lost. ᶜ Of which only 6.8 were recovered, 12 assumed lost.

In both runs at 350° and in the test at 400°, approximately 200 moles of products were recovered from the cracking of 100 moles of hexadecenes. Practically all of the reaction taking place, therefore, must have been primary. At 450°, on the other hand, of the 200 moles formed by the primary reactions, 50 were cracked in secondary reactions, making it difficult to determine which products are primary and which secondary. For the other three runs, however, a reasonably complete picture of the primary reactions can be given, as shown in Table VI.

The parenthetical figures given for the 400° experiment represent alternate reactions which would also agree with the experimental results, but which would correspond to the different secondary reactions also shown in parentheses. Still others could be devised, but there is no basis for preferring any one set of secondary reactions. Since the amount of secondary reaction is small, however, the over-all picture of the primary reaction is not greatly altered.

The values given in Table VI are in excellent agreement with the molar values given in Table V. The close agreement between the results found for the cetene and the low boiling hexadecenes shows that the products derived from cetene are the same as those from the i-hexadecenes, and confirms the conclusion that the cracking of the former is preceded by isomerization.

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Table VI

Reactions Occurring in Cracking of Cetene

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Primary cracking reaction	Moles reacting per 100 moles of cetene cracked			Secondary cracking reaction	Moles of primary product reacting per 100 moles of cetene cracked at 400°
	350°	350°[a]	400°		
$C_{16} \longrightarrow H_2 + C_{16}$	0.0	0.4	0.0		
$C_{16} \longrightarrow C_1 + C_{15}$	0.0	0.3	0.0		
$C_{16} \longrightarrow C_2 + C_{14}$	2	0.2	2		
$C_{16} \longrightarrow C_3 + C_{13}$	9	6	10		
$C_{16} \longrightarrow C_4 + C_{12}$	20	20	12 (17)		
$C_{16} \longrightarrow C_5 + C_{11}$	16	19	17	$C_{11} \longrightarrow C_5 + C_6$	6
$C_{16} \longrightarrow C_6 + C_{10}$	15	18	19 (17)	$C_{10} \longrightarrow C_4 + C_6$ ($C_{12} \longrightarrow 2C_6$)	2 (2)
$C_{16} \longrightarrow C_7 + C_9$	22	20	24		
$C_{16} \longrightarrow 2C_8$	17	14	16 (13)	$C_8 \longrightarrow 2C_4$ ($C_{12} \longrightarrow 3C_4$)	6 (3)

[a] Charging stock: isomerized hexadecenes.

The distillation curves (obtained with a 17-plate vapor-jacketed column[14]) for the hydrogenated gasolines produced at 400 and 450° (Figs. 4 and 5) show plateaus at the same temperatures; but the lower plateaus are broader and the higher plateaus narrower in the 450° curve, corresponding to more secondary cracking of the higher-boiling primary products. This increase in the amount of low-boiling products is probably also responsible for the higher octane numbers found for both the unsaturated and the hydrogenated gasolines produced at 450°, as compared with the 400° product (see Table IV).
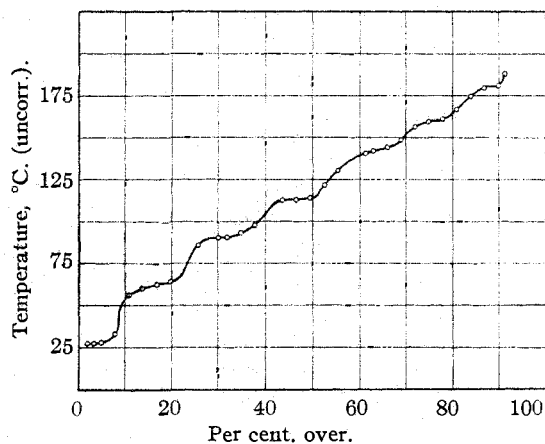

Fig. 4.—Distillation of hydrogenated gasoline from catalytic cracking of cetene at 400°.

The plateaus in the distillation curves indicate the presence of isopentane (28°), 2-methylpentane (60°) and possibly 3-methylpentane (63°) and 2,3-dimethylbutane (58°), the methylhexanes (90–92°) and possibly 2,3-dimethylpentane

(14) Tongberg, Quiggle and Fenske, Ind. Eng. Chem., 26, 1212 (1934).

(90°), the methylheptanes (117–119°) and possibly 2,3-dimethylhexane (116°), the methyloctanes (about 142°), the methylnonanes (about 160–165°) or dimethyloctanes (about 156–160°), and the methyldecanes or dimethylnonanes (about 175–183°). The refractive indices and boiling points obtained at 450° are given in Table VII.
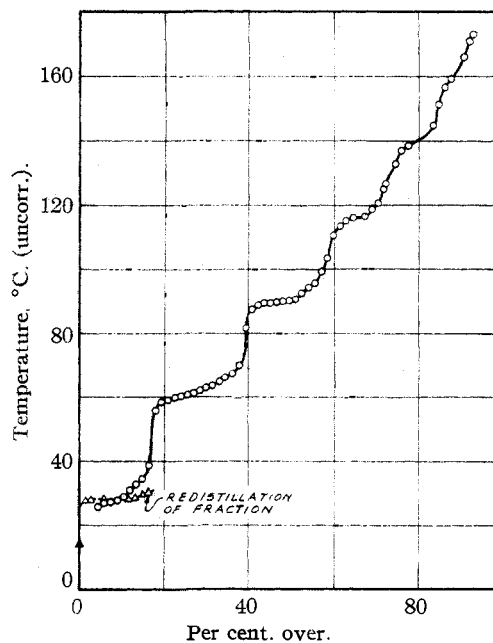

Fig. 5.—Distillation of hydrogenated gasoline from catalytic cracking of cetene at 450°.

It is significant that no appreciable amounts of normal paraffins were present in any fraction of the gasoline, showing that both fragments resulting from the cetene cracking are isomerized. Since thermal scission of an olefin molecule may be expected[4] to occur chiefly at the bond β to the double bond (an observation borne out in this

TABLE VII

SUGGESTED COMPD. IN GASOLINE OBTAINED FROM CETENE AT 450°

		Found		Literature (11)	
Compound	B. p., °C. (uncorr.)	$n^{20}D$		B. p., °C.	$n^{20}D$
Isopentane	27.8–28.2	1.3543		28.0	1.3552
2-Methylpentane	59.2–60.0	1.3730–1.3736		60.2	1.3717
3-Methylpentane	63.8–64.0	1.3755		63.2	1.3765
2-Methylhexane	89.4	1.3880		90.0	1.3851
3-Methylhexane	90.0	1.3889		91.8	1.3887
2,3-Dimethylhexane	115.6	1.3999		115.8	1.4015
4-Methylheptane	116.4	1.4007		118.0	1.4035
3-Methylheptane	120.2	1.4020		119.0	1.3982
(3-Ethylhexane)				118.6	1.4014

catalytic work by the absence of appreciable quantities of gaseous products containing fewer than three carbon atoms) and since it is further apparent from Table VI that scission takes place to an almost equal extent at each C—C bond of the molecule (except at the three bonds nearest each end of the chain) we may conclude that cetene is catalytically cracked chiefly according to the following successive steps: (1) isomerization of cetene to lower-boiling branched-chain hexadecenes, either with or without migration of the double bond; (2) scission of the chain to an almost equal extent at each bond except those near the extremities of the molecule; (3) isomerization of any normally liquid olefinic products to isoölefins; and (4) with longer contact times or at higher temperatures, secondary decomposition of the longer-chained primary products as in steps 2 and 3, so that the products having fewer than eight carbon atoms increase in amount, while those having more than eight carbon atoms decrease in amount.

It should further be pointed out that small amounts of paraffinic products are formed, and that corresponding to these there should also be either diolefins (not necessarily conjugated), acetylenes, cyclo-olefins, or aromatics in the product. Alternatively a small amount of carbon deposit on the catalyst accounts for the liberation of sufficient hydrogen to hydrogenate a portion of the olefinic product.

Cracking of *n*-Octane.—The previous work on the catalytic and pyrolytic decomposition of *n*-octane has already been adequately summarized.[15,16] In none of the catalytic work were refractory oxide catalysts employed; of the pyrolytic work, that of Marschner[16] is the most complete and was carried out under temperature conditions similar to the present work, so that his results are comparable.

The catalytic decomposition of *n*-octane was carried out at 525, 540, 555 and 570°, at a liquid space velocity of four volumes of liquid octane per volume of catalyst per hour. The results are summarized in Table VIII.

TABLE VIII

CATALYTIC CRACKING OF *n*-OCTANE

Furnace temp., °C.	525	540	555	570
Duration, hr.	0.5	0.5	0.5	0.5
Space velocity	4.1	4.3	4.2	4.2
n-Octane charged, g.	144	152	147	147
Liquid recovered, g.	141	148.4	142	138
Weight % of charge	1.8	2.7	4.0	5.4
Volume, liters (N. T. P.)	2.0	2.9	4.1	5.7
Molecular weight	34.5	36.8	36.5	36.7
H_2	16.3	15.1	12.9	9.0
CH_4	34.9[a]	32.5[c]	8.8	6.1
C_2H_4	20.3	15.0	13.3	12.6
C_2H_6			7.2	7.0
C_3H_6	26.7[b]	32.4[b]	20.4	34.5
C_3H_8			16.5	11.5
i-C_4H_8	2.0	7.3	5.1	6.1
n-C_4H_8			12.4	8.5
C_4H_{10}			3.5	4.9
Unaccounted, wt. % of charge	0.0	−0.7	−1.0	0.0

(with left-bracket labels: Gaseous product[d], Anal., vol. %)

[a] Total paraffins; index 2.30. [b] Includes *n*-butenes. [c] Total paraffins; index 2.51. [d] Does not include gas dissolved in the liquid product which may amount to 1–2% of the octane charged.

Because of the small amount of reaction and of materials used, a complete analysis of the products was made only in the case of the 570° run. The results are shown in Table IX, together with comparable thermal results calculated from the data of Marschner.

TABLE IX

CATALYTIC AND PYROLYTIC CRACKING OF *n*-OCTANE

		Catalytic	Marschner, pyrolytic
Furnace temp., °C.		570	570
Contact time, seconds		1.0	12.7
Decompn., %		11.0	19.4
Moles of products per mole of octane cracked		2.4	3.2
Complete product analysis, moles per 100 moles of octane cracked	H_2	13	0.3
	CH_4	9	77
	C_2H_4	19	86
	C_2H_6	11	55
	C_3H_6	52	46
	C_3H_8	18	6.5
	C_4H_8	22	18
	C_4H_{10}	7	1.3
	C_5	73	15
	$C_6 + C_7$	16	21
Unaccounted, wt. % of charge		2.2	0.8

Although the degree of cracking in the two runs differs considerably, a comparison is justifiable because of Marschner's conclusion that for pyro-

(15) Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publishing Co., New York, 1937.
(16) Marschner, *Ind. Eng. Chem.*, **30**, 554 (1938).

lytic decomposition "the product analyses were the same when decomposition was increased from 18 to 33%, . . . and differed but little from those obtained at 538°" where 11% cracking was obtained. Furthermore, the incomplete analyses of Dintzes and Zherko[17] for 13% conversion at 570° check closely those of Marschner for 19% decomposition at the same temperature, indicating that essentially the same reactions occur over a rather wide range of temperature and conversion.

It is clear from Table IX that the pyrolytic cracking results in a greater yield of methane, ethane and ethylene than the catalytic reaction, and a far smaller yield of C_5–C_7 hydrocarbons and of hydrogen. Furthermore, from the work of Marschner and of Dintzes and Zherko, it is estimated that to attain a pyrolytic cracking of 11% at 570°, a contact time of seven or eight seconds would be necessary. The catalyst therefore shortens the time of the reaction seven- to eightfold. It is also significant that the n-octenes decomposed so much more easily over the catalyst that at 375° there was twice as much cracking as with n-octane at 570° with comparable feed rates.

Cetane Cracking.—The cracking of cetane has been studied both thermally[12,18] and catalytically[19] by Gault and his associates, who concluded that in the absence of catalysts the carbon chain was broken indiscriminately at any point, but that with rising temperature the point of scission approached the chain end. The use of quartz or pumice tube-packing lowered the cracking temperature somewhat. This temperature lowering is probably due to more efficient heat transfer to the reacting system rather than to any catalytic properties of the quartz or pumice. The catalysts studied by Gault were of the metallic (e. g., nickel) type so that the reactions produced involved the carbon–hydrogen bonds rather than the carbon–carbon bonds. Such catalytic results are not comparable with the present work.

In the present study cetane was cracked catalytically at 500° and liquid space velocity four. Because of the small amount of reaction and the limited amount of cetane available, the cetane recovered from the first pass (boiling in the original boiling range) was recycled and that recovered

(17) Dintzes and Zherko, J. Gen. Chem. (U. S. S. R.), **6**, 68 (1936).

(18) Gault and Barmann, Ann. combustibles liquides, **1**, 77 (1926); Gault and Hessel, Compt. rend., **179**, 171 (1924); Ann. chim., (10) **2**, 319 (1924).

(19) Gault and Sigwalt, Ann. combustibles liquides, **2**, 309, 543 (1927).

from the second pass was further recycled. The low-boiling liquid products of the three passes were combined and hydrogenated; the gases were separately analyzed, but showed substantially the same composition. The composite results are shown in Tables X and XI.

TABLE X

CATALYTIC CRACKING OF CETANE AT 500° (COMPOSITE OF THREE PASSES)

Duration, hr.	8.74
Space velocity, cc./cc. cat./hr.	4.0
Total cetane charged, g.	2728
Liquid product (b. p. >10°), wt. % of charge	88.5
Gasoline, b. p. 10–200°, wt. % of charge	6.9
Intermediate fraction, b. p. 200° (750 mm.) – 144° (13 mm.)	3.6
Cetane, b. p. 144-147° (13 mm.)	76.4
Bottoms	1.6
Gaseous product	
Weight % of charge	11.1
Volume, liters (N. T. P.)	147
Molecular weight	48
Unaccounted, wt. % of charge	0.4

TABLE XI

PRODUCTS OF CETANE CRACKING

Product	Volume %		Moles per 100 moles of cetane decompd.
H_2	1.5		3.7
CH_4	1.7		4.2
C_2H_4	1.0		2.4
C_2H_6	2.0		4.9
C_3H_6	32.8	Gas	80
C_3H_8	12.6		31
i-C_4H_8	11.5		28
n-C_4H_8	21.0		51
C_4H_{10}	16.0		39
C_5	42		41
C_6	28	Gasoline	25
C_7	11		8.3
C_8-$C_{12}{}^a$	19		11.4
C_{13}-$C_{15}{}^b$			18.5

[a] Assumed molecular weight, 130. [b] Assumed molecular weight, 196.

From the fact that approximately 350 moles of reaction products was formed from 100 moles of cracked cetane, it is apparent that these are not the primary products, and no definite reaction mechanism can be postulated. It is interesting, however, that every mole reacting yielded approximately one mole each of C_3, C_4 and gasoline boiling-range hydrocarbons, indicating a selectivity of the catalyst for the formation of three-carbon and four-carbon fragments. In this respect the results differ from those of Gault[12,18] on thermal cracking, since his products led him to conclude that the initial step in the decomposition

was the breaking-off of terminal groups forming methane and ethylene. Although exact comparisons with Gault's work are not possible due to the incompleteness of his data, it appears that in the experiments carried out in empty and packed tubes higher temperatures or longer contact times were required to attain the degree of cracking found in our experiments.

The preponderance of small molecules in the present study and the analytical data indicate either that the primary reaction products are more unstable than cetane itself, and that they are 75 to 100% decomposed to secondary products as compared with the 20% decomposition of cetane, or that the cetane molecule is ruptured at several points simultaneously.

The greater stability of n-octane as compared with cetane is indicated by the 11% decomposition of the former with the same catalyst and space velocity at a temperature 70° higher (570°) than that required to produce 20% decomposition of cetane.

The hydrogenated gasoline from the cetane decomposition had an A. S. T. M. octane number of 70. Distillation of this hydrogenated product on a 17-theoretical plate column of the vapor jacket[14] type, gave the curve shown in Fig. 3 and indicated the presence of isopentane (b. p. 28°), n-pentane (b. p. 36°), 2-methylpentane (b. p. 60°), n-hexane (b. p. 60°), and 2-methylhexane (b. p. 90°); 3-methylhexane (b. p. 92°) and 2,3-dimethylpentane (b. p. 90°) also may be present. No n-heptane appeared to be present; higher boiling constituents could not be determined because of the small amount of gasoline available. Isopentane, isohexane and isoheptane were all present in greater amounts than the corresponding normal compounds.

Experimental Part

Materials.—n-**Butenes** were prepared by the dehydration of butanol-2 over activated alumina. Low-temperature fractionation showed the following percentage composition: C_3 hydrocarbons 0.2, butene-1 fraction 15.2, butene-2 fraction 83.8, C_5 and higher 0.8. A small amount of isobutene and butanes may also have been present; the C_4 fraction showed 1.8% absorption in 64% sulfuric acid and 95% absorption in 87% sulfuric acid.

Pentene-1 was prepared from a selected cut (134.0–135.8°) of Eastman Technical pentanol-1 by dehydration over activated alumina at 400°. The pentene fraction was separated from the unreacted amyl alcohol and redistilled over sodium hydroxide in a 50-bubble cap column of the Bruun type.[10] The fraction used in this work boiled at 28–31°, and had a refractive index n^{20}D 1.3720, as com-

pared with the literature value of n^{20}D 1.3711.[20] After hydrogenation the refractive index was n^{20}D 1.3574 as compared with the literature value for n-pentane of n^{20}D 1.3576. Distillation with a column of 17 theoretical plates efficiency, however, showed the presence of a maximum of 12.5% of isopentane and a minimum of 87.5% of n-pentane.

n-**Octenes and n-Octane.**—The n-octenes used in the experiments at 385 and 400° were prepared by the dehydration of capryl alcohol over activated alumina at 400° and purified by distillation through a Hempel column. The distillation curve with a small laboratory column of 5 to 10 theoretical plates[21] is shown in Fig. 1. Approximately 10% boiled below 121°, and 7.5% above 125°; the refractive index was n^{20}D 1.4131. The n-octenes used in the experiment at 375° were the fraction of the above octenes boiling at 121.2–124.9°, and had an index of refraction n^{20}D 1.4133.

The n-octane was prepared by hydrogenation of the Hempel cut of n-octenes, and had a refractive index n^{20}D 1.3978, as compared with the value[11] of 1.3980. The melting point was −58°.

Cetane.—Dupont Diesel Standard cetane was used without further purification.

Cetene.—Dupont cetene (technical) was redistilled *in vacuo* in a Claisen flask fitted with a 6-inch (15-cm.) Vigreux side-arm, and the fraction boiling at 148–151° at 7 mm. (d_4^{20} 0.778) was employed in this work; 13.5% of lower-boiling and 12% of higher-boiling material were discarded. All of the vacuum distillations analyzing the products were made in the same Claisen flask as that described above.

Experimental Procedure.—The charging stock was pumped by a copper-bellows pump[22] to an electrically heated preheater of stainless steel tubing maintained at such a temperature that the emergent vapor was at the reaction temperature, and thence into a 100-cc. stainless steel reaction chamber filled with 6–10 mesh granules of catalyst in a bed 15 cm. long. Although the catalyst chamber was supported in an electrically heated aluminum-bronze block which was maintained at a temperature constant to within ±1°, the actual temperature of the catalyst bed (which was read with a movable iron–constantan thermocouple) varied considerably because of the character of the reaction. For example, in the run with cetene at 450°, the reaction was endothermic and a temperature drop of 40° existed between the top of the bed and a point near the bottom. In the pentene run, however, there was a temperature rise in the first portion of the catalyst bed followed by a temperature drop so that although the furnace was maintained at 400°, the actual catalyst temperature varied between 448 and 370°. In the butene runs a temperature rise was observed also. A number of hypotheses have been considered to explain these unexpectedly large temperature changes, but as yet none of them is satisfactory.

The reaction products were led through a water condenser and a vertical ice reflux condenser fitted above a

(20) Leendertse, Tulleners and Waterman, *Rec. trav. chim.*, **53**, 715 (1934).

(21) Thomas, Bloch and Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

(22) Tropsch and Mattox, *Ind. Eng. Chem.*, **26**, 1338 (1934).

receiving flask for the liquid product. The gases were analyzed by a combined low-temperature fractionation and absorption analysis. In the analysis of the butenes 63% sulfuric acid was used to absorb isobutene and 87% acid the n-butenes. The condensable portion of the gases was collected in a dry-ice–trichloroethylene trap, and the C₅ and higher-boiling hydrocarbons recovered by a low-temperature distillation with the column previously described.[21] The dissolved gas was removed from the liquid product by the same column and separately analyzed, although in some cases a weighted composite sample of all the gaseous products was analyzed. Maleic anhydride absorption was used in butadiene determination.[23]

Summary

A number of hydrocarbons cracked at atmospheric pressure in the presence of an activated silica–alumina catalyst showed the following behavior:

1. A mixture of n-butenes underwent extensive catalytic isomerization to isobutene in the temperature range 385 to 600°, accompanied by polymerization and cracking. Between 450 and 600° the isobutene content of the C₄-product was 24.1 ± 1.5%.

2. n-Pentenes showed reactions similar to those of the butenes, yielding 50% of isopentenes at 400°.

3. A mixture of n-octenes underwent both catalytic isomerization to isoöctenes and catalytic cracking to gaseous products consisting principally of equal amounts of normal and isobutene.

The results are consistent with the theory that isomerization precedes cracking. In the temperature range 375 to 400° the conversion was over 80%.

4. The primary catalytic reaction of cetene in the range 300 to 450° was isomerization to isohexadecenes; the secondary reaction was cracking to lower-boiling olefins, accompanied by isomerization of normal olefinic products to isoolefins. The isohexadecenes catalytically cracked approximately three times as rapidly as cetene itself.

5. n-Octane catalytically cracked seven to eight times as rapidly as in thermal decomposition, and the catalytic products contained more C₅–C₇ hydrocarbons and less methane, ethane, and ethylene than the pyrolytic products. The temperature required for the catalytic cracking of octane was 200° higher than that required for n-octenes.

6. Cetane was catalytically cracked largely to C₃, C₄ and C₅ hydrocarbons. The gasoline boiling-range products contained both branched-chain and straight-chain hydrocarbons, in contrast to the products of cetene cracking, which were essentially all branched-chain.

Although the behavior in thermal cracking of cetane and cetene is quite similar, cetane is far more stable toward catalytic cracking than cetene. In both cases, the products of catalytic cracking are quite different from those of pyrolytic cracking.

(23) Tropsch and Mattox, *Ind. Eng. Chem., Anal. Ed.,* **6**, 104 (1934).

The Adsorption of Hydrogen by Copper Dispersed in Calcium Oxide

BY JOHN R. LEWIS, LAWRENCE J. E. HOFER AND HOWARD WHITEHEAD

Recently a paper[1] by Lewis and Taylor appeared in which the data for the adsorption of hydrogen by copper dispersed in magnesia were given. Papers by Joris, Verhulst and Taylor[2] and by Taylor and Joris[3] showed (1) that copper, when prepared by the method[1] of Lewis and Taylor, is highly dispersed in magnesia, and (2) that this dispersed copper is an excellent catalyst for hydrogenation reactions.

Because of the chemical similarity of magnesia and calcium oxide, one would expect that calcium oxide, like magnesia, would be an excellent dispersing medium for copper and therefore adsorption measurements and catalytic studies on copper dispersed in calcium oxide would prove to be of special interest.

This paper presents the data for the adsorption of hydrogen (1) on pure calcium oxide, and (2) on copper dispersed in calcium oxide.

Experimental

Apparatus.—The apparatus used for this work is a modified form of that used in Princeton for similar investigations.

Gases.—Hydrogen was prepared by the electrolysis of a 15% sodium hydroxide solution using nickel electrodes,

(1) Lewis and Taylor, THIS JOURNAL, **60**, 877 (1938).
(2) Joris, Verhulst and Taylor, *Bull. soc. chim. Belg.,* **46**, 393 (1937).
(3) Taylor and Joris, *ibid.,* **46**, 241 (1937).