tent dropped to 6.48%. The product had no melting point. The orange precipitate obtained at stage (C) weighed 1.20 g. Purified as before, the nitrogen content was found to be 7.57%. After several reprecipitations the nitrogen content found was 6.84%.

Compound $C_{18}H_{16}N_2$.—The residue left upon the evaporation of the chloroform–petroleum ether at stage (D) of the procedure, after recrystallization from methanol, yielded 0.54 g. of white plates melting at 82°; insoluble in water but soluble in the usual organic solvents.

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.2; H, 6.21; N, 10.54. Found: C, 83.1, 83.1; H, 6.21, 6.29; N, 10.78, 10.84.

A picrate formed readily in alcohol solution which, recrystallized from alcohol, melted at 157°.

2-Propyl-4-phenyl-5-hydroxyglyoxaline.—To a solution of 9.12 g. (0.06 mole) of phenylglyoxal hydrate and 7.35 g. (0.06 mole) of butyramidine hydrochloride in 500 ml. of water was added 4.5 ml. of 50% potassium hydroxide solution (0.06 mole). The solution turned yellow and a precipitate gradually formed. After twenty-four hours the precipitate was filtered off (A). The precipitate, weighing 6.4 g., was recrystallized from a mixture of methanol and ethyl acetate. The colorless prisms obtained were slightly soluble in dilute base, the lower alcohols, butyl acetate and insoluble in water, ethyl acetate or the hydrocarbons. The compound gradually decomposed at 215–230°.

Anal. Calcd. for $C_{12}H_{14}ON_2$: C, 71.2; H, 6.98; N, 13.87. Found: C, 71.0, 70.9; H, 6.97, 6.99; N, 13.90, 13.94.

A picrate formed in alcohol solution and was recrystallized from alcohol; m. p. 183.5–184°.

Anal. Calcd. for $C_{12}H_{14}ON_2 \cdot C_6H_3O_7N_3$: C, 50.1; H, 3.95; N, 16.24. Found: C, 50.1, 50.3; H, 4.30, 4.34; N, 16.38.

A hydrochloride, prepared in the manner described above, melted at 182–184°.

Anal. Calcd. for $C_{12}H_{14}ON_2 \cdot HCl$: N, 11.73. Found: N, 11.49, 11.48.

The filtrate (A) was neutralized and allowed to stand another twenty-four hours. A yellow precipitate weighing 0.22 g. was formed. The product dissolved in chloroform and precipitated with petroleum ether gave a pale yellow powder with no definite melting point (4.28% nitrogen). No other product could be isolated from the solution.

The following general procedure gives good yields of the glyoxalines only. To a water solution containing 0.1 mole of the amidine hydrochloride and 0.1 mole of phenylglyoxal hydrate in 750 ml. of water was added 37 ml. of 50% potassium hydroxide (0.5 mole). The solution was then allowed to stand from two to four hours at room temperature. The resulting yellow solution then was treated with carbon, filtered, and carefully neutralized with hydrochloric acid. A voluminous precipitate formed as the neutral point was approached. The precipitate was filtered off, washed with water and dried. The yield for acetamidine was 72%, for propionamidine was 69% and for butyramidine was 75%. The crude products were pure enough for ordinary purposes.

The absorption spectra data here reported were obtained using a Hilger E3 spectrograph and a Hilger sectorphotometer. A high frequency underwater spark served as a light source. The photographic plates were Eastman III-O and Panchromatic.

Summary

1. A 2-methyl-4-phenyl-5-hydroxyglyoxaline was prepared and derivatives characterized.

2. A 2-ethyl-4-phenyl-5-hydroxyglyoxaline was prepared and derivatives characterized.

3. A 2-propyl-4-phenyl-5-hydroxyglyoxaline was prepared and derivatives characterized.

4. A compound, $C_{17}H_{14}N_2$, probably a pyrimidine, was isolated and studied.

5. A compound, $C_{18}H_{16}N_2$, probably a pyrimidine, was isolated and studied.

6. A compound, $C_{24}H_{19}O_5N$, of unknown structure was isolated and derivatives prepared.

7. Absorption spectra data are reported.

APPLETON, WIS. RECEIVED JULY 5, 1944

[CONTRIBUTION FROM UNIVERSAL OIL PRODUCTS CO.]

Hydrocarbon Reactions in the Presence of Cracking Catalysts. II.[1] Hydrogen Transfer

BY CHARLES L. THOMAS

While studying the practical applications of catalytic cracking, it was found that when an olefin-containing gasoline that had been produced by catalytic cracking was again brought in contact with the cracking catalyst the olefin content of the gasoline decreased whereas the isoparaffins and aromatics increased. This action suggested that hydroaromatic hydrocarbons were present in the gasoline and that these lost hydrogen to form the aromatic hydrocarbons while the hydrogen thus made available, reacted with isoolefins present to form isoparaffins. Consequently, the reaction was called *hydrogen transfer.* It was found that the hydrogen transfer reaction could be aided by adding higher boiling (above about 200°) petroleum fractions that should contain appreciable quantities of cycloparaffins.[2]

Certain of the results obtained with gasolines were not readily explainable by such a simple hypothesis. More hydrogen seemed to be used in saturating olefins than was available from the cycloparaffins present, so the cycloparaffins appeared to be helpful if present but not essential. Earlier work[1] had indicated that under some conditions minor proportions of paraffinic products could be formed from olefins in the presence of this type of catalyst. It was suggested that some of the hydrogen needed to convert the olefins to paraffins was made available by the formation of a hydrogen-deficient catalyst deposit.

The present article describes a test of this hypothesis which comprises subjecting *n*-octenes

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(1) For the first article in this series see G. Egloff, J. C. Morrell, C. L. Thomas and H. S. Bloch, THIS JOURNAL, **61**, 3571 (1939).

(2) E. H. Kanhofer (to Universal Oil Products Co.) U. S. Patent 2,275,441 (March 10, 1942).

to the action of a cracking catalyst under conditions which give chiefly paraffinic products.

Experimental

***n*-Octenes.**—The *n*-octenes were prepared as previously described.[1] The properties were as follows: n^{20}_D 1.4138; d^{20}_4 0.7216; specific dispersion, $(n^{20}_F - n^{20}_C)/d^{20}_4 \times 10^4 =$ 119.5; bromine number = 134; boiling range = 120.0 to 122.6°.

Catalyst.—The silica–alumina–zirconia catalyst was prepared according to the procedure of Thomas and Lee.[3] Twelve hundred cubic centimeters of a commercial water glass (9% sodium oxide, 28.5% silicon dioxide) was diluted with 12 liters of distilled water. Dilute hydrochloric acid was prepared by mixing 420 cc. of 12 *N* acid and 1580 cc. of distilled water. The sodium silicate solution was agitated while 1600 cc. of the dilute acid was added gradually. A silica hydrogel formed which was broken up by the agitator. Three liters of water was added, followed by 300 cc. of acid. The silica hydrogel was collected on a filter and pressed to remove adhering liquid. The filter cake was broken up and slurried, with agitation, in 10 liters of distilled water and again collected on a filter. This last operation was repeated five times. Two additional washes of the same type were made in which 45 cc. of 12 *N* hydrochloric acid was added to each 10 l. of distilled water before the silica hydrogel was added. The final filter cake assayed 12.3% silicon dioxide.

The purified silica hydrogel, 913 g., was suspended in 2500 cc. of distilled water, 124 g. of zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) and 18 g. of aluminum chloride ($AlCl_3 \cdot 6H_2O$) were dissolved in 500 cc. of water and this solution was added to the silica hydrogel and thoroughly agitated; 472 cc. of normal ammonium hydroxide was gradually added. The composite was collected on a filter, washed with distilled water until substantially free of chloride ions, and dried at 110°. The dried product was formed into cylinders 3.17 by 3.17 mm. (1/8 in. × 1/8 in.) by a pelleting machine. After calcining for one hour at 800° the pellets were ready for use.

TABLE I

ANALYSIS OF GASEOUS PRODUCTS IN MOLE PER CENT.

H_2	1.4
CH_4	2.9
C_2H_4	0.6
C_2H_6	1.7
C_3H_6	11.6
C_3H_8	11.2
i-C_4H_8	5.4
n-C_4H_8	11.9
C_4H_{10}	53.2

Procedure.—The apparatus and procedure used were the same as those employed in the previous work, except that the apparatus was slightly modified by the use of a high-pressure reciprocating pump, a pressure regulator-recorder at the exit end of the reactor tube, and a pressure gage and rupture plate in the line between the pump and the inlet (upper) end of the reactor.

During one hour 286 g. of the octenes was passed over 400 cc. (320 g.) of catalyst at 375° and 8 kg. per sq. cm. pressure. The products obtained, expressed as weight per cent. of the octenes charged, were: gas, 12.9%; liquid, 79.3%; catalyst deposit, 12.6%; and unaccounted gain, 4.8%.

Analytical Methods.—The gases collected as such during each run and the gases collected by debutanization of the liquid products were analyzed by the methods reported previously.[1] The analysis is given in Table I. Debutanization of the liquid was conducted with a short column fitted with a 10-in. spiral of nichrome[4] and a dry-ice–acetone condenser. A vapor-jacketed column[5] packed with single-turn glass helices which had an efficiency of 17 theoretical plates was used for the distillation of all the liquid products.

The liquid product cuts were analyzed by the procedure and method of calculation described in U. O. P. Method No. H-173-40,[6] which is based on the methods of Grosse and Wackher[7] and of Thomas, Bloch and Hoekstra.[4] In calculating the olefin- and aromatic-free refractive indices, the following values were used:

B. p. of fraction, °C.	Assumed n^{20}_D of— Olefins	Aromatics
40–70	1.3930	. . .
70–95	1.4022	1.5012
95–125	1.4128	1.4969
125–150	1.4221	1.4988

In calculations involving the fractions boiling above 150°, it was arbitrarily assumed that the average molecular weight was 168 (that of $C_{12}H_{24}$). The paraffin and naphthene contents of these cuts were not separately estimated. For calculating their limiting aromatic contents, it was arbitrarily assumed that if monocyclic, the aromatics in these cuts had an average specific dispersion, $\delta = 165$, and if bicyclic, $\delta = 250$. The analysis of the liquid product is given in Table II.

TABLE II

ANALYSIS OF LIQUID PRODUCT

Fraction	B. p., °C.	Wt., %	d^{20}_4	n^{20}_D	δ[d]	Br. no.	% Olef.	% Arom.	% Par.	% Naph.
C_5	10–40	13.5	0.627	1.3585	103	50	22	0	78	0
C_6	40–70	5.4	.655	1.3785	108	53	28	0	72	0
C_7	70–95	3.6	.687	1.3923	105	44	27	0	63	10
i-C_8	95–120	51.2	.708	1.4020	104	41	28	0	64	7
n-C_8	120–125	4.0	.720	1.4090	110	50	35	4		
C_9	125–150	5.8	.761	1.4308	122	33	26	22	51	1
Bottoms	>150	16.6	.841	1.4798	149	17	18[a]	31–71[b]	11–51[b]	
Total liquid							26	7–13	55–63[c]	4–13[c]

[a] As C_{12}. [b] Depending upon whether aromatics are mononuclear or binuclear. [c] Sum of paraffins + cycloparaffins ≧ 61%. [d] δ = Specific dispersion = $(n^{20}_F - n^{20}_C)/d^{20}_4 \times 10^4$.

The catalyst deposit was analyzed for carbon and hydrogen by subjecting a sample of the used catalyst to combustion. This result is given in Table III. A part (27.6%) of

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(3) C. L. Thomas and E. C. Lee (to Universal Oil Products Co.), U. S. Patent 2,347,648 (May 2, 1944).

(4) C. L. Thomas, H. S. Bloch and J. Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

(5) C. O. Tongberg, D. Quiggle and M. R. Fenske, *Ind. Eng. Chem.*, **26**, 1212 (1934).

(6) "U. O. P. Laboratory Test Methods for Petroleum and its Products," Universal Oil Products Company, Chicago, 1940, pp. H-45–H-59.

(7) A. V. Grosse and R. C. Wackher, *Ind. Eng. Chem. Anal. Ed.*, **11**, 614 (1939).

the catalyst deposit was removed by exhaustively extracting the catalyst with benzene. A part of the benzene extract was soluble in acetone and a part was insoluble. The acetone soluble part (40%) was a dark, viscous oil while the insoluble part was a reddish-brown solid which melted at 195–210°. It dissolved in benzene or chloroform with an intense red-green fluorescence.

TABLE III

ANALYSIS OF CATALYST DEPOSIT

Material	Wt. % carbon	Wt. % hydrogen	Mol. wt. (ebullioscopic)	Formula calculated
Spent catalyst	9.34	1.03		$CH_{1.31}$
Benzene extract, acetone insoluble	92.97	6.82	396 431	$CH_{0.875}$
Benzene extract, acetone soluble	91.68	8.46	202 224	$CH_{1.10}$
Extracted catalyst	6.89	0.819		$CH_{1.42}$

The analysis of the extracted oil and solid as well as the material remaining on the catalyst after extraction are given in Table III.

Discussion of Results

It is clear from Table I that a major proportion of the gaseous products is paraffinic. Simple cracking of *n*-octenes was shown[1] to give olefins. The analyses of the liquid products, Table II, also shows a major proportion of paraffinic products. It is obvious that hydrogen transfer has occurred in the absence of added hydrogen donors. Certain other reactions have also occurred.

1. Isomerization.—Note in Table II that the iso-C_8 fraction constituted 93% of the C_8 cut.
2. Scission of Carbon–Carbon Bonds.—This reaction accounts for the gaseous products. Note the tendency of the catalyst to form selectively C_3 and C_4 gaseous products rather than C_1 and C_2 gases.
3. Polymerization or Condensation to Form Products Containing More than Eight Carbon Atoms.—These products included higher boiling liquid products as well as the catalyst deposit.
4. Cyclization.—Aromatics within the boiling range of the xylenes, as well as still higher boiling aromatics, were found. The formation of the aromatics may have been preceded by the formation of the corresponding cycloparaffin. The evidence for the presence of the cycloparaffins is less convincing than that for the aromatics.

In order to understand the reaction better it is desirable to make a hydrogen balance covering the reaction products. Since all olefinic material, either original octenes or olefinic products have the same hydrogen content, *i. e.*, C_nH_{2n}, the hydrogen balance need be concerned only with the non-olefinic reaction products and the octenes that reacted to produce non-olefinic products. Therefore the "number of moles of non-olefinic products formed per hundred moles of octenes converted to non-olefinic products" forms a convenient basis for the hydrogen balance. A hydrogen balance on this basis is presented in Table IV.

From this table it can be seen that there are two major sources of the hydrogen which converted the olefins into paraffins: (a) the conversion of a part of the olefins into aromatics, and (b) the conversion of a part of the olefins into a hydrogen-poor catalyst deposit. Before this observation was made, there had been a tendency to regard the catalyst deposit as a necessary nuisance which resulted from side reactions. The present work established the fact that the catalyst deposit can be formed as an integral part of the reaction, and the products associated with its formation are often desirable. In the present experiment the catalyst deposit accounted for at least 50% of the hydrogen needed to convert the olefins into the paraffins found.

TABLE IV

HYDROGEN BALANCE IN OCTENE CONVERSION

Non-olefinic products[a]	Moles per 100 moles of octenes converted to non-olefinic products
Paraffins	100–105
Cycloparaffins	12–7
Aromatics[b]	11
Aromatics[c]	7.8
Hydrogen required to form paraffins	100–105
Hydrogen available from aromatic formation[b]	33
Hydrogen available from aromatic formation[c]	42
Hydrogen available from catalyst deposit formation[d]	52

[a] 1.73 g. moles of octenes was converted to gaseous and liquid non-olefinic products exclusive of the catalyst deposit. [b] Assuming that all aromatics are monocyclic. [c] Assuming that the aromatics boiling up to 150° are monocyclic, and those boiling higher bicyclic. [d] The catalyst deposit is 10% hydrogen or $(C_3H_4)_n$ so that $3_nC_8H_{16} \rightarrow 8(C_3H_4)_n + 16_n(H)$.

The detailed study on *n*-octenes reported here was carried out with a silica–alumina–zirconia catalyst. Similar results have been obtained with technical hydrocarbon mixtures with synthetic silica–alumina and silica–zirconia catalysts.[8]

There are processes[9,10] for making aviation fuels in which gasolines containing olefins are contacted with cracking catalysts at temperatures in the range of 350 to 525° and at pressures somewhat above atmospheric to produce an improvement in the antiknock quality. The olefin content of the gasoline is reduced, the aromatic content increased, and the susceptibility to lead tetraethyl improved. The reactions described in the present work aid in understanding the chemistry of these processes.

Acknowledgment.—The author wishes to thank Mr. George Hervert for preparing the *n*-octenes

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(8) C. L. Thomas (to Universal Oil Products Co.), U. S. Patent 2,328,754 and 2,328,755 (September 7, 1943).

(9) C. L. Thomas (to Universal Oil Products Co.), U. S. Patent 2,328,756 (September 7, 1943).

(10) C. L. Thomas, N. K. Anderson, H. A. Becker and J. McAfee, *Oil and Gas J.*, **42**, 27, 131 (1943); *Petroleum Refiner*, **22**, 365 (1943); *Natl. Petroleum News*, **35**, R-570 (1943).

and Dr. T S. Ma of the University of Chicago for the micro-analyses.

Summary

1. Using *n*-octenes as the starting material it has been shown that a synthetic cracking catalyst can cause hydrogen transfer in the absence of added cycloparaffins.

2. The hydrogen transfer resulted in the formation of paraffin and aromatic hydrocarbons and a carbonaceous catalyst deposit poor in hydrogen.

3. At least 50% of the hydrogen needed to account for the paraffins found came from the catalyst deposit.

4. Reactions of isomerization, cyclization and polymerization or condensation accompanied the hydrogen transfer reaction.

CHICAGO, ILL. RECEIVED APRIL 7, 1944

[CONTRIBUTION FROM UNIVERSAL OIL PRODUCTS CO.]

Hydrocarbon Reactions in the Presence of Cracking Catalysts. III. Cyclohexene, Decalin and Tetralin

BY HERMAN S. BLOCH AND CHARLES L. THOMAS

Synthetic cracking catalysts were shown to have isomerized olefins and to have severed carbon–carbon bonds of paraffins and olefins.[1,2] It was of interest to examine the reactions of cycloölefins and cycloparaffins in the presence of these synthetic catalysts.

Frost[3] stated that naphthenes cracked in the presence of aluminosilicate catalysts to form olefins, and that the olefins isomerized and decomposed to produce gasolines containing branched chain hydrocarbons. No experimental data were given so that it is not clear whether Frost used pure hydrocarbons or naphthenic petroleum fractions.

The present work describes the reactions at atmospheric pressure of cyclohexene[4] in the presence of a synthetic silica–alumina–thoria catalyst and the reactions of decalin and tetralin in the presence of a synthetic silica–alumina–zirconia catalyst. The conditions of the experiments and a summary of the product distribution are given in Table I. Table II shows the composition of the gaseous products. The liquid products were examined, by methods described in the experimental part, in sufficient detail to permit a semi-quantitative estimation of the principal reaction products or types of product, so that a picture could be drawn of the principal reactions and of the effect on them of the operating variables studied.

Cyclohexene.—The reactions of cyclohexene were studied at constant liquid hourly space velocity (volumes of liquid charge per gross catalyst volume per hour) and approximately constant ratio of hydrocarbon charged to catalyst weight, with temperature as the principal variable. The estimated composition of the liquid products is shown in Table III.

From the data of Table III, it is evident that the principal reactions of cyclohexene, in order of decreasing magnitude, were isomerization, polymerization and hydrogen transfer. These reactions occurred at all three temperatures, and the extent of all of them increased with rise in temperature, within the range studied. In addition, ring scission, which was absent or negligible at 250 and 300°, became more definite at 400°.

The isomerization of cyclohexene yielded methylcyclopentenes. Unidentified methylcyclopentenes were previously reported as cyclohexene isomerization products with titanium oxide or beryllium oxide catalysts at 450°.[5] In our work, two isomers were identified among the reaction products: methylcyclopentene-1 and methylcyclopentene-2. The former was present in much greater quantity than the latter, indicating that isomers having substituents attached to olefinic carbon atoms were formed most readily.[6] Although no evidence of the other two isomers was found, it does not seem unlikely that small quantities of methylcyclopentene-3 were formed.

At 300°, 70% of the cyclohexene that reacted was isomerized. It is clear that the reaction conditions can be controlled to make this reaction predominate. At 400°, more methylcyclopentane was isolated than methylcyclopentenes. The presence of such large amounts of methylcyclopentane in the reaction products and such small amounts of cyclohexane is taken as an indication that isomerization of cycloolefins is a more rapid reaction than hydrogen transfer; however, the situation is not clear-cut, because of the possi-

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(1) G. Egloff, J. C. Morrell, C. L. Thomas and H. S. Bloch, THIS JOURNAL, **61**, 3571 (1939).

(2) C. L. Thomas and H. S. Bloch, U. S. Patents 2,216,284 and 2,216,285 (October 1, 1940); U. S. Patent 2,328,753 (September 7, 1943).

(3) A. V. Frost, *J. Phys. Chem.* (U. S. S. R.), **14**, 1313 (1940).

(4) C. L. Thomas and H. S. Bloch, U. S. Patent 2,333,903 (November 9, 1943).

(5) Yu. A. Arbusov, and N. D. Zelinsky, *Compt. rend. acad. sci.* URSS, **30**, 717-720 (1941).

(6) That such isomers are the most stable was shown for pentenes by R. H. Ewell and P. E. Hardy, THIS JOURNAL, **63**, 3463 (1941); for hexenes by F. C. Whitmore and P. L. Meunier, *ibid.*, **55**, 3721 (1933) and by P. L. Cramer and A. L. Glasebrook, *ibid.*, **61**, 230 (1939); and for olefins more generally by G. B. Kistiakowsky, *et al.*, *ibid.*, **58**, 137 (1936).