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Dehydrocyclization of *n*-Hexane on a Bifunctional Catalyst

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Dehydrocyclization of *n*-hexane was investigated in the temperature range 400–500°C, pressure range 3–20 atm, and at space velocities 10–150 (g feed/g cat × hr) on a commercial Pt/Al_2O_3 catalyst in a fixed bed reactor. From product distributions of the individual conversions of *n*-hexane, 1-hexene, 2-methylpentane, 2-methyl-1-pentene, 1,5-hexadiene, and methylcyclopentane at the same reaction conditions and from experiments with variation of residence time at constant temperature and pressure, a reaction mechanism for the dehydrocyclization of *n*-hexane is proposed, in which at least four different reaction paths for the aromatization are possible: 5- and 6-membered ring closure and cyclization of *cis*-2-hexene and 1,5-hexadiene.

INTRODUCTION

The catalytic dehydrocyclization of paraffins has been widely studied, and several reaction mechanisms have been proposed. It is difficult to compare these mechanisms because (1) gas phase product distributions are used to study a reaction occurring on the catalyst surface; (2) the product consists of a large number of components, which finally depends on the accuracy of the analysis; (3) it is very difficult to distinguish between intermediates important for the investigated reaction and other components; and (4) different reaction mechanisms may occur at different active sites of the catalyst. Paál and Tétényi (*1–3*) described their results for the dehydrocyclization of *n*-hexane over platinum, nickel, and metal oxide catalysts by analogous mechanisms via the intermediates hexene–hexadiene–hexatriene–benzene. Gault and co-workers (*4,5*) postulated a 5-membered ring-closure of the paraffin over nonacidic platinum catalysts. Davis (*6,7*) reported evidence for direct C_6 ring-closure over nonacidic platinum and chromia catalysts. Kazanskii *et al.* (*8,9*) obtained results which could be explained by both C_5 and C_6 ring-closure over platinum catalysts and a mechanism via olefins and diolefins over metal oxide catalysts. Other authors (*10–12*) explained their results by mechanisms similar to those discussed above.

In the present study information on the mechanism of the catalytic dehydrocyclization of *n*-hexane was obtained from analysis of product distributions of the individual reactions of *n*-hexane, 1-hexene, 2-methylpentane, 2-methyl-1-pentene, 1,5-hexadiene, and methylcyclopentane.

EXPERIMENTAL METHODS

(*a*) *Apparatus and Selection of Operation Conditions*

The experiments were carried out in an isothermally operated flow reactor designed for pressures up to 60 atm, temperatures up to 600°C, and space velocities up to 300 LHSV. The apparatus was similar to the one described in a preceding paper

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(*13*). In all experiments the molar ratio of hydrogen to hydrocarbon was about 6. Up to five samples were analyzed for every experimental point. Changes in catalyst activity were checked by reference runs. The catalysts were activated in H_2 atmosphere in two steps at temperatures up to 500°C.

When selecting suitable conditions for the investigation of the reaction mechanism of the dehydrocyclization of *n*-hexane to form benzene, rather strong restrictions are encountered. In order to obtain olefinic intermediates in measurable concentrations, the reactions have to be performed at temperatures above 400°C depending on the total pressure. With rising temperatures the aromatization, which is a highly endothermic reaction, is favored as well. At temperatures above 500°C and with increasing partial pressures at a constant hydrogen–hydrocarbon molar ratio, the reactions of *n*-hexane, hexane isomers, and methylcyclopentane yielding hydrocracking products become the governing reactions. In the temperature range in which the experiments have to be performed, high hydrogen partial pressures are necessary to prevent catalyst deactivation resulting from coke deposition and from long-chain polymers, which are formed, for example, from methylcyclopentane, from becoming the dominating parameter. Following numerous preliminary tests, the experiments for the investigation of the dehydrocyclization of *n*-hexane were performed with a Pt/Al_2O_3 catalyst in the temperature range 450–500°C, at pressures between 3 and 20 atm, with a hydrogen–hydrocarbon molar ratio of 6 and at residence times ranging from 0.8 to 12×10^{-2} [g cat × hr/g HC].

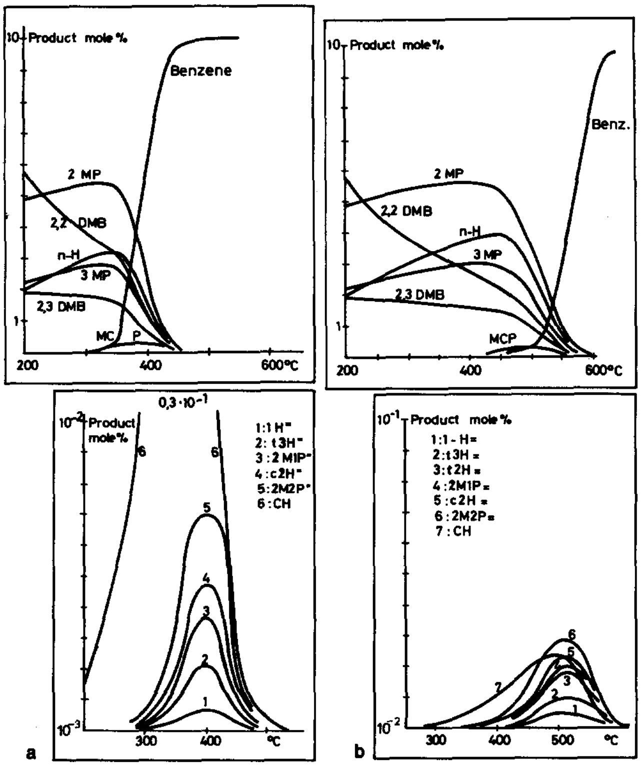

FIG. 1. Equilibrium concentration for C_6-hydrocarbons as a function of temperature, H/C ratio 26/6; (a) pressure, 3 atm; (b) pressure, 20 atm.

(*b*) *Catalyst and Materials*

Sinclair Baker catalyst (acidic Al_2O_3 containing 0.6 wt% Pt) from Kali-Chemie-Engelhard (cyclindrical particles, diameter 1.5 mm, length 2–4 mm); *n*-hexane (99% GC), Merck AG; 1-hexene (95% GC), methyl-cyclopentane (99% GC), Fluka AG; 2-methyl-1-pentene (95% GC), 2-methylpentane (99% GC), 1,5-hexadiene (99% GC), Ega Chemie.

(*c*) *Analysis*

A gas chromatograph with a capillary column (length 50 m) filled with squalene was used to analyze the reactor effluent samples. The following hydrocarbons have been detected with this system: C_1–C_5 alkanes and alkenes; 2,2-dimethylbutane, 3-methyl-1-pentene, 1,5-hexadiene, 2,3-dimethylbutane, 2-methylpentane, 2-methyl-1-pentene, 1-hexene, 3-methylpentane, trans-3-hexene, 2-methyl-2-pentene, *trans*-2-hexene, *n*-hexane, cis-2-hexene, *trans*-3-methyl-2-pentene, methyl-cyclopentane, benzene, 1-methyl-1-cyclopentene, 1,3-cyclohexadiene, cyclohexane, cychlohexene, and 1,4 cyclohexadiene. The C_6-hydrocarbons mentioned here represent more than 99% of the C_6-hydrocarbons found in the different reactor effluents. The peak areas were computed by an integrator.

RESULTS

1. *Calculation of Equilibrium Concentrations*

Assuming that isomerization, dehydrogenation, and cyclization reactions of

TABLE 1

PRODUCT DISTRIBUTIONS AND REACTION CONDITIONS FOR THE CONVERSION OF HYDROCARBONS (MOLE%)[a]

Feed	MCP	2M1P$^=$	1H$^=$	1,5$^{==}$	2MP	2MP	*n* − H	*n* − H
p(atm)	3	3.1	3.0	3.4	3.0	3.1	3.0	3.0
T(°C)	500	500	500	500	500	500	500	500
W/F(g hr/g) 10^2	2.3	2.6	2.6	2.7	2.6	10.3	2.5	10
H_2/HC	6	6	6	6	6	6	6	6
$C_1 + C_2$	0.1	0.9	0.5	0.6	0.7	2.6	0.6	3.3
C_3	0.07	0.9	0.9	1.8	0.6	2.2	0.7	3.6
C_4	0.07	2.7	1.7	1.0	1.4	4.7	0.8	5.9
C_5	0.05	1.4	0.5	1.4	0.9	2.8	0.4	2.9
2,2 DMB	0.04	0.7	0.3	0.3	3.1	4.9	0.6	2.8
3M1P$^=$	—	1.3	0.4	0.4	0.2	0.2	0.1	0.2
1,5H$^{==}$	0.3	2.9	.05	21.0	0.6	0.5	0.2	0.5
2,3DMB	0.07	1.5	0.6	1.4	3.4	4.4	0.8	2.4
2MP	0.7	16.7	4.6	3.6	64.0	31.8	5.8	13.2
2M1P$^=$	0.05	22.2	0.7	1.1	0.9	0.7	0.2	0.5
1H$^=$	—	1.2	18.2	4.3	—	—	0.2	0.3
3MP	0.5	6.8	4.4	3.3	11.0	15.5	5.3	10.2
t3H$^=$	—	1.5	6.7	5.1	0.3	0.5	1.1	0.9
2M2P$^=$ + t2H$^=$	—	22.7	11.1	10.4	1.4	1.5	1.5	1.7
n − H	2.1	5.7	35.8	12.9	5.2	11.2	73.3	35.7
c2H$^=$	0.6	3.0	7.2	4.4	0.7	1.2	0.5	0.9
t3M2P$^=$	0.05	3.2	1.6	2.2	0.7	1.0	0.4	0.7
MCP	81.6	1.8	1.3	2.5	1.7	3.4	2.9	3.1
Benzene	7.6	0.7	1.3	4.8	2.4	9.6	3.8	10.5
1M1CP$^=$	4.9	0.4	0.3	4.1	0.2	0.5	0.4	0.4
1,3CH$^{==}$	0.05	—	0.1	2.9	—	—	—	—
1,3,5H$^{===}$	—	—	—	—	—	—	—	—

[a] M = methyl. P = pentane. H = hexane. H$^=$ = hexene. H$^{==}$ = hexadiene. P$^=$ = pentene. C = cyclo. B = butane. $C_{1...5}$ = hydrocarbons with 1. . . 5 carbons.

n-hexane are fast compared with the hydrocracking reaction, which is justified under the reaction conditions chosen, equilibrium concentrations of the C_6-system (C_6-paraffins, C_6-olefins, cyclohexane, methylcyclopentane, benzene) are calculated by minimizing the free energy of the total system (*14,15*). The results shown in Fig. 1 reveal that the maximum olefin concentrations are in a range of 0.001–0.05 mole% depending on system temperature and pressure. These values are far lower than those measured during the corresponding experiments (Table 1), indicating that olefins are intermediate products in the isomerization and cyclization of *n*-hexane.

2. *Hydrogenolysis and Dehydroisomerisation of Methylcyclopentane*

The product distribution (Table 1) shows that the concentrations of 1,5-hexadiene, *cis*-2-hexene, and 1-methyl-1-cyclopentene exceed by far the values of the equilibrium concentrations. The concentrations of other olefinic hydrocarbons

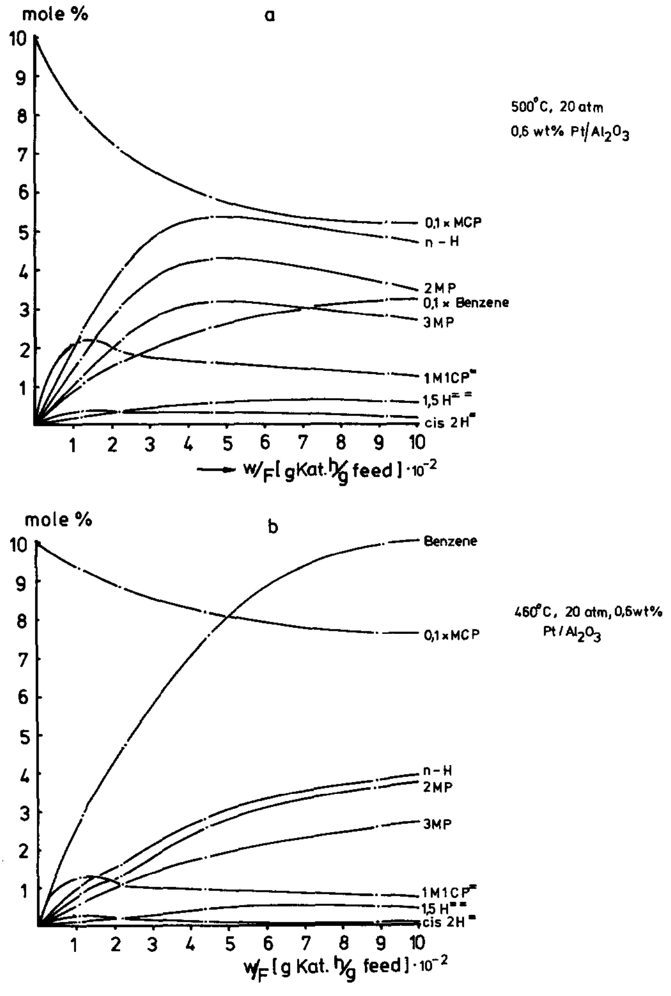

FIG. 2. Product composition from methylcyclopentane as a function of residence time.

are less than 0.05 mole% and *n*-hexane is the main product formed by the hydrogenolysis of methylcyclopentane. The concentrations of 2-methylpentane and 3-methylpentane are approximately $1/3$–$1/4$ that of *n*-hexane, and the concentrations of 2,2-dimethylbutane and 2,3-dimethylbutane are $1/30$–$1/40$ the *n*-hexane concentrations.

The effect of residence time on reaction rate and product distribution for two different temperatures (Fig. 2a,b) was determined at a total pressure of 20 atm instead of 3 atm. This was necessary to prevent catalyst deactivation from becoming the dominant parameter, which completely covers the effect of the other reaction variables on yield and product distribution. The 1-methyl-1-cyclopentene concentration passes through a maximum in both diagrams. As in the experiments discussed before, *cis*-2-hexene and 1,5-hexadiene are the only unsaturated paraffins found in measurable amounts in the product. The cyclic olefins detected were 1-methyl-1-cyclopentene and in some product samples 1,3-cyclohexadiene.

3. *Reactions of 1-Hexene, 1,5-Hexadiene, 2-Methyl-1-Pentene, 2-Methylpentane, and n-Hexane*

The main reactions (Table 1) of 1-hexene are hydrogenation to yield hexane and isomerization of the double bound. Methylpentenes are formed only in small concentrations. The conversion of 1-hexene yields fewer cyclic products than that of *n*-hexane, 1,5-Hexadiene, 1-methyl-1-cyclopentene, and 1,3-cyclohexadiene are present in the product gas. 1,3,5-Hexatriene could not be detected. The conversion of 1,5-hexadiene (Table 1) yields about equal amounts of all hexene isomers, and as with 1-hexene, the concentrations of these isomers are considerably higher than those of the methylpentenes. About 12% of the total yield are cyclic compounds with quite high amounts of 1-methyl-1-cyclopentene and 1,3-cyclohexadiene.

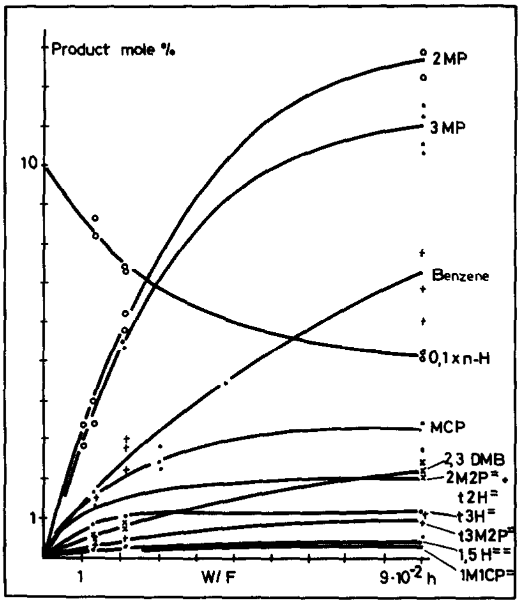

FIG. 3. Product composition from *n*-hexane as a function of residence time; temperature, 500°C; pressure, 20 atm; catalyst, 0.6 %wt Pt/Al_2O_3).

The relative yield of methylcyclopentane and benzene is considerably higher when converting 2-methylpentane and *n*-hexane as compared to the conversion of 2-methyl-1-pentene and 1-hexene. With an increase in residence time, the methylcyclopentane–benzene ratio is shifted toward benzene as methylcyclopentane dehydroisomerization is increased as well. It is remarkable that the individual conversions of *n*-hexane and 2-methylpentane yield methylcyclopentane and benzene in amounts of the same magnitude. This fact is valid, too, for the formation of hexenes and methylpentenes.

In Fig. 3 the product distribution from *n*-hexane conversion is plotted as a function of residence time. Both curves representing the formation of methylcyclopentane and benzene have nonzero slopes when the residence time approaches zero.

This means the two components are formed by different mechanisms.

DISCUSSION

From the product distribution for the conversion of methylcyclopentane one concludes that hydrogenolysis proceeds along two main reaction paths: (1) via methylcyclopentane-ring opening yielding *cis*-2-hexene and (2) via 1-methyl-1-cyclopentene and 1,5-hexadiene, since *cis*-2-hexene and 1,5-hexadiene are the only C_6-unsaturates detected. Considering the product distributions from the individual conversions of 1,5-hexadiene and 1-hexene, *cis*-2-hexene formation by 1,5-hexadiene hydrogenation or 1,5-hexadiene formation by *cis*-2-hexene dehydrogenation can be excluded. 1,5-Hexadiene hydrogenation yields all C_6-olefins in about the same amounts; hexene is dehydrogenated to yield hexadiene only in a very small degree. *Cis*-2-hexene and 1,5-hexadiene formation via hydrogenating ring opening of methylcyclopentane to yield adsorbed hexanes and consecutive dehydrogenation can also be excluded, since all C_6-unsaturates concentrations in the product should be of the same magnitude, as can be seen from the conversions of *n*-hexane and methylpentane, whereas only *cis*-2-hexene and 1,5-hexadiene were produced by converting methylcyclopentane. The large quantity of *n*-hexane relative to those of the methylpentanes supports the discussed reaction paths of the methylcyclopentane ring opening reaction, since hydrogenation yielding hexane are the favoured reactions of hexene and hexadiene.

Provided the two ring-opening reactions are reversible, one can conclude that on the tested catalyst *cis*-2-hexene and 1,5-hexadiene cyclization is favored relative to the cyclization of the other C_6-unsaturates.

In addition to the reaction paths discussed for the dehydrocyclization of *n*-hexane, others can be derived by comparing the measured product distributions of the conversions of *n*-hexane, 2-methylpentane, 2-methyl-1-pentene, and 1-hexene.

The fact that the conversion of C_6-paraffins yields much higher amounts of cyclic products than the conversion of C_6-olefins at identical reaction conditions allows the conclusion that direct C_5- and C_6-ring closure are the main reaction paths of *n*-paraffin cyclization. Ring closure to yield cyclopentyl- and cyclohexyl-intermediates proceeds at about the same rate, as can be deduced from the nearly identical yields of methylcyclopentane and benzene when converting methylpentane and *n*-hexane and from the product distributions at short residence times when converting *n*-hexane (Fig. 3).

With an increase in residence time more methylcyclopentane is converted to benzene, which is thermodynamically more stable at that temperature. As can be observed from the product distributions measured as a function of residence time for converting methylcyclopentane (Fig. 2), 1-methyl-1-cyclopentene is the principal intermediate. At 460 and 500°C the concentrations of 1-methyl-1-cyclopentene run through a well-defined maximum. Isomerization of 1-methyl-1-cyclopentene to yield a cyclohexene is rate controlling for the dehydroisomerization of methylcyclopentane to benzene, since cyclohexene and cyclohexadiene could be detected only in traces in most reactor effluents. This means that dehydrogenation is fast relative to isomerization.

From the results discussed, it is obvious that dehydrocylization of *n*-hexane on a bifunctional Pt/Al_2O_3 catalyst proceeds by a very complicated reaction mechanism, in which cyclization can occur by direct C_5- or C_6-ring closure of *n*-hexane and hexane isomers or by ring closure of the olefins formed by dehydrogenation of *n*-hexane and its isomers.

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