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Dealkylation, Fragmentation, and C_5 Dehydrocyclization of 3-Phenylpentane on Silica-Alumina Catalyst

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An investigation was undertaken into the catalytic conversions of 3-phenylpentane on a silica-alumina catalyst in the temperature interval of 410° to 490°C and at space velocities of 0.86 to 3.23 hr^{-1}.

It was established that the reactions of dealkylation, fragmentation, and dehydrocyclization take place under the conditions investigated, and an assumption is stated relative to the mechanisms of these reactions. A carbonium ion with a positive charge in the nucleus is formed as an intermediate product of dealkylation, a carbonium ion with a positive charge in the side chain being formed upon fragmentation and dehydrocyclization.

Dehydrocyclization is accompanied by the formation of the pentacyclic ring of α-ethylindane which, under the conditions of the process, is isomerized to β-methyl-1,2,3,4-tetrahydronaphthalene and, following the latter's dehydrogenation, is converted into β-methylnaphthalene.

INTRODUCTION

The individual monoalkylbenzenes are of considerable interest as model compounds for investigating the chemistry and mechanism of the catalytic processes, the cracking of hydrocarbons on silica-alumina catalysts included.

The systematic investigations carried out by Kazanskii and one of the authors of the present article (*1*, *2*) with monoalkylbenzenes whose side chains included two, three, and four carbon atoms indicate that the principal reaction during the catalytic cracking of these hydrocarbons on a silica-alumina catalyst is the breaking off of the side chain from the benzene ring with the formation of benzene and of an olefin corresponding to the structure of the side chain. The dealkylation of isopropylbenzene to benzene and propylene, for instance, has such a selective course that it has long become a model reaction for the kinetic investigations of heterogeneous processes in a flow, for determining the activity of various natural and synthetic silica-aluminas, as well as for studying the nature of the active centers and the mechanism of the silica-alumina catalysts.

One of the authors of this article and Pelova (*3*) recently established, using certain modern methods of analyzing complex hydrocarbon mixtures, that upon cracking *n*-amylbenzene on silica-alumina catalyst the reaction of dehydrocyclization with formation of β-methylnaphthalene takes place parallel with the basic reaction of dealkylation. Related to this former reaction is also the almost complete hydrogenation of the olefin in which the carbonium ion from the broken-off side chain is stabilized.

The reaction of dehydrocyclization of monoalkylbenzenes with three and more carbon atoms in the side chain to naphthalene or indane structures has been observed by other authors upon using oxide or metal catalysts (*4–11*), and more recently nickel sulfide deposited on silica-alumina has been used to this end (*12*).

In our present work we decided to investigate the catalytic conversions of 3-phenylpentane, whose structure does not permit the direct course of C_6 dehydrocyclization. The results of such an investigation can cast additional light on the problem of the structure of the side chain in the molecule of the monoalkylbenzenes, on the rate of the reaction of dealkylation, as well as on the problem of the chemistry and mechanism of the reaction of dehydrocyclization in the presence of silica-alumina catalyst.

APPARATUS AND PROCEDURE

The catalytic cracking of the monoalkylbenzene investigated was carried out in a quartz reactor with a 20-mm diameter contained in a furnace with heat-adjustment device. The temperature in the reactor was maintained with a precision of ±1°C and was read by means of a thermocouple contained in the catalyst layer. The hydrocarbon was fed into the reactor by means of an injector operated by a synchronous motor. The length of the time of experiments was 1 hr for chemical investigation of the process and 15 min for kinetic investigations. The liquid products of cracking of 3-phenylpentane were collected in a receptacle cooled with running water and ice, while the gaseous products were collected in a gasometer.

The contact used was 10 ml of silica-alumina catalyst of the Houdry type in the form of cylinders (4×4 mm) with the following composition: SiO_2, 86.91%; Al_2O_3, 10.65%; MgO, 0.70%; and oxides of Fe, Pb, and Zn, 1.70%.

Liquid hourly space velocity (LHSV) signifies the hourly volume of liquid reactant per volume of catalyst.

The products of the cracking of 3-phenylpentane were analyzed by means of precise rectification, gas-liquid chromatography, infrared, ultraviolet, and Raman spectra.

The rectification was carried out on a column with effectiveness of 36 theoretical plates.

The chromatographic analyses were carried out with the "Fractovap" apparatus, model B, manufactured by the Carlo Erba Company of Italy. To analyze the gaseous products of the hydrocarbon fractions with boiling point below that of benzene we used the following: a column 4 m long and 0.6 cm in diameter, support, Rysorb; stationary phase, dimethylformamide 30% of the weight of the support; temperature, 0°C; transporting gas, nitrogen with a velocity of 60 ml/min. The analysis of the catalysates and of the fractions from them with b.p. up to 190°C was carried out under the following conditions: column 2 m long and 0.6 cm in diameter; support, Rysorb; stationary phase, Reoplax, 15% of the weight of the support; transporting gas, nitrogen with velocity 60 ml/min; temperature, according to the temperature of the fraction investigated. The fraction with b.p. over 190°C was likewise analyzed in a 2-m column 0.6 cm in diameter, though the stationary phase was polyethylene glycol adipate, 8% of the weight of the support (ground unglazed tile).

The Raman spectra were taken with a three-prism glass spectrograph ISP-51; the infrared spectra, on the UR-10 apparatus; and the ultraviolet ones, on the Leres apparatus.

The initial hydrocarbon was synthesized by us. From ethyl benzoate and ethyl bromide after Grignard we obtained 3-phenylpentanol (*13*) which, upon reduction with hydroiodic acid (*14*), was converted into 3-phenylpentane. Following rectification, the chromatographically pure 3-phenylpentane used during our present work possessed the following constants: b.p. 68.0°C/12 mm; n_D^{20} 1.4895; d_4^{20} 0.8640. Data from pertinent literature (*15*): b.p. 80.5°C/20 mm; n_D^{20} 1.48851; d_4^{20} 0.86104.

The α-ethylindane necessary for identifying the cracking products was synthesized after Grignard (*16*). From α-indanone and ethyl bromide we obtained the respective carbinol, which was dehydrated by heating under reflux condenser to α-ethylindene (n_D^{20} 1.5544) and the latter was hydrated over platinum oxide to α-ethylindane. After rectification, the α-ethylindane synthesized possessed the following constants: b.p. 68°C/4 mm; n_D^{20} 1.5250. Data from pertinent literature: b.p. 93°C/12 mm; n_D^{20} 1.5235.

TABLE 1

RESULTS FROM THE RECTIFICATION OF THE CATALYSATE OBTAINED FROM THE CRACKING OF 3-PHENYLPENTANE

Boiling temperature (°C/760 mm)	Weight % of the catalysate
Gas (B)	1.48
20.0–27.9°	4.95
27.9–37.0°	5.99
37.0–40.5°	6.12
40.5–79.3°	6.06
79.3–80.3°	31.38
80.3–97.3°	3.14
97.3–186.0°	7.15
186.0–187.0°	28.99
187.0–190.0°	2.37
Residue	2.37

RESULTS

Six consecutive experiments were carried out at a temperature of 490°C and a space velocity of 0.86 hr^{-1} and the material balance from them is the following: catalysate, 85.2%; gas (A), 9.3%; and coke, 5.5%. Prior to rectification the catalysate was stabilized at room temperature and an additional amount of gas (B) was obtained from it.

The catalysate from the six experiments was divided by means of precise rectification into 11 fractions boiling within narrower temperature intervals, the first one of which represents the gas (B) separated from the catalysate. The data related to the percentage content of these fractions are given in Table 1. The gaseous and liquid products obtained were subjected to chromatographic and spectrum analyses.

Concentrations of the identified individual products of the cracking of 3-phenylpentane expressed as mole percentages of the number of gram moles of the hydro-

TABLE 2

PRODUCT DISTRIBUTIONS FROM THE CRACKING OF 3-PHENYLPENTANE AT CATALYST TEMPERATURE 490°C AND SPACE VELOCITY 0.8 HR^{-1}

Products	Products in moles/100 moles of reactant	Products	Products in moles/100 moles of reactant
Methane and hydrogen	26.8	Benzene	66.2
Ethane	0.2	Toluene	0.6
Ethylene	3.4	Ethylbenzene	1.5
Total C_2 hydrocarbons	3.6	*n*-Propylbenzene	1.5
		sec-Butilbenzene	0.8
Propane	0.6	Total C_{7-11} alkylbenzenes	3.0
Propylene	7.2		
Total C_3 hydrocarbons	7.8	3-Phenylpentane	28.6
		α-Methylindane	1.2
Butane	0.2	α-Ethylindane	0.4
Isobutane	0.2	2-Methyltetralin(1, 2, 3, 4)	0.2
Butene-1	0.7	Naphthalene	0.2
Butene-2(*trans*)	1.0	β-Methylnaphthalene	0.4
Butene-2(*cis*)	1.2	α-Methylnaphthalene	0.2
Isobutene	2.3	Dimethylnaphthalene	0.1
Total C_4 hydrocarbons	5.6	Total bicyclic products	2.7
n-Pentane	0.5		
Isopentane	7.0		
n-Pentene-1	1.4		
Pentene-2(*trans*)	6.4		
Pentene-2(*cis*)	3.4		
2-Methylbutene-1	5.6		
2-Methylbutene-2	11.4		
3-Methylbutene-1	0.8		
Total C_5 hydrocarbons	36.5		

carbon passed over the catalyst, are given in Table 2.

The data contained in Table 2 show that under the conditions investigated 71.4% of the initial reactant has undergone changes as a result of which 32 new individual products were obtained. Nineteen of them are paraffin and olefin hydrocarbons with an open carbon chain: Five are monocyclic aromatic hydrocarbons; seven are bicyclic aromatic hydrocarbons with indane, tetralin, and naphthalene structures; hydrogen and unreacted 3-phenylpentane were also found.

Benzene and C_5 hydrocarbons are represented in the largest amounts among the products of cracking.

The catalytic conversions of 3-phenylpentane were likewise investigated separately at three different temperatures and at four different space velocities for each temperature. The results of this investigation are systematized in Table 3.

TABLE 3

PROCESS CONDITIONS AND YIELDS OF AROMATIC PRODUCTS EXPRESSED AS MOLE PERCENTAGES OF THE NUMBER OF GRAM MOLES OF THE REACTANT PASSED OVER THE CATALYST

Conditions		Products			
T (°C)	LHSV	Benzene	Alkylbenzene C_7-C_{10}	3-Phenylpentane	Bicyclic proucts d
490°	0.86	68.0	1.6	26.0	2.0
	1.32	60.1	1.1	29.3	1.7
	1.84	57.0	0.9	34.4	1.4
	3.23	52.5	0.3	40.0	0.4
450°	0.86	60.0	0.6	29.0	1.6
	1.32	48.3	0.4	40.0	0.9
	1.84	36.2	0.2	55.1	0.8
	3.23	31.0	0.1	60.4	0.8
410°	0.86	40.0	0.3	52.0	1.2
	1.32	29.4	0.2	51.1	0.9
	1.84	24.3	0.2	63.0	0.8
	3.23	21.4	0.1	69.2	0.7

The data contained in Table 3 show that upon changing the temperature in the interval between 410° and 490°C and the space velocities in the interval from 0.86 to 3.23 hr^{-1} the general character of the catalytic conversions of 3-phenylpentane on silica-alumina catalyst is preserved.

DISCUSSION OF THE RESULTS

The large number of different chemical products obtained as a result of the catalytic conversions of 3-phenylpentane on silica-alumina catalyst indicates that the cracking of the alkyl aromatic hydrocarbon investigated is a complex aggregate of parallel and consecutive reactions.

It has been established by means of labelled carbon atoms in the ring and side chain of *n*-amylbenzene (*16*) that the side chain which breaks off from the benzene ring takes an active part in the formation of the products deposited on the surface of the catalyst during the cracking of alkyl aromatic hydrocarbons in the presence of silica-alumina catalysts—products referred to under the general designation of "coke." On the other hand, the benzene ring is perfectly stable under the conditions of catalytic cracking and undergoes no changes with breaking the carbon–carbon bonds building it. This makes it possible to judge for the initial conversions of 3-phenylpentane in the first place from the nature and amount of the aromatic hydrocarbons obtained.

In our instance the mole percentages of the aromatic hydrocarbons obtained correspond approximately to the mole percentages of the changed 3-phenylpentane. In the light of these facts and taking into consideration the nature of the aromatic hydrocarbons obtained, the changes undergone by 3-phenylpentane under the conditions investigated by us most probably take the following three paths:

First—breaking off the side chain from the benzene ring and formation of benzene and C_5 olefins;

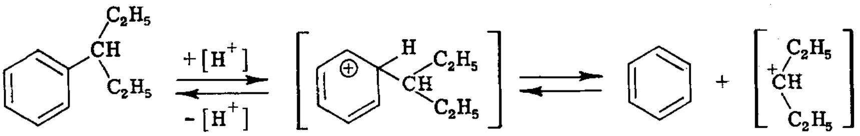
Second—distribution of the carbon–carbon bonds in the side chain and formation of monoalkylbenzenes whose molecules have a smaller number of carbon atoms than that of 3-phenylpentane: toluene, ethylbenzene, *n*-propylbenzene, and *sec*-butylbenzene; and

Third—closing of a second ring with

formation of an indane structure, ethylindane in particular.

The first path is the predominant one. Out of the 71.4% 3-phenylpentane which has undergone changes at a temperature of 490°C and a space velocity of 0.86 hr^{-1}, 90.4% has undergone dealkylation, 6.1% has joined the reaction of fragmentation, and 3.5% the reaction of dehydrocyclization.

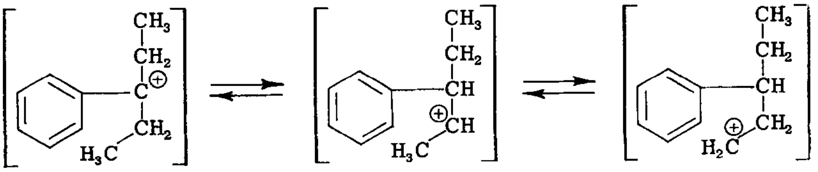
On the basis of the experimental data accumulated about the velocity of dealkylation of monoalkylbenzenes of various structures of the side chain (*1, 2*) and in view of the acid character of the silica-alumina catalyst, it would be logical to assume that the dealkylation of 3-phenylpentane is an electrophilic substitution of the alkyl radical with a proton from the catalyst and its course is on the pattern of the following diagram:



The calculation made with the equation of Frost (*17*) on the basis of benzene yields from experiments with various temperatures and various space velocities shows that the apparent activation energy of the dealkylation reaction of 3-phenylpentane is 18 300 cal/mole. This value is appreciably lower than that of the activation energy for the dealkylation of *n*-amylbenzene, 32 000 cal/mole (3) and is of the order of the value calculated for the dealkylation of isopropylbenzene, 17 500 cal/mole. The value of the apparent activation energy of 3-phenylpentane dealkylation found by us is in agreement with the ionic mechanism of the reaction referred to above.

The amyl carbonium ion which has broken off from the benzene ring is the source for the formation of the olefin and paraffin hydroccarbons. Among the hydrocarbons with five carbon atoms in the molecule the amount of those with the iso structure is nearly twice as big as the amount of the hydrocarbons with normal chains. This is indicative of the fact that the amyl carbonium ion and the olefins in which it is stabilized undergo considerable isomerization under the conditions of the reaction. Besides that the total amount of the C_5 hydrocarbons is 36.5 mole%, whereas the amount of benzene is 66.2 mole%, i.e., it is obvious that together with isomerization these hydrocarbons also undergo a secondary cracking.

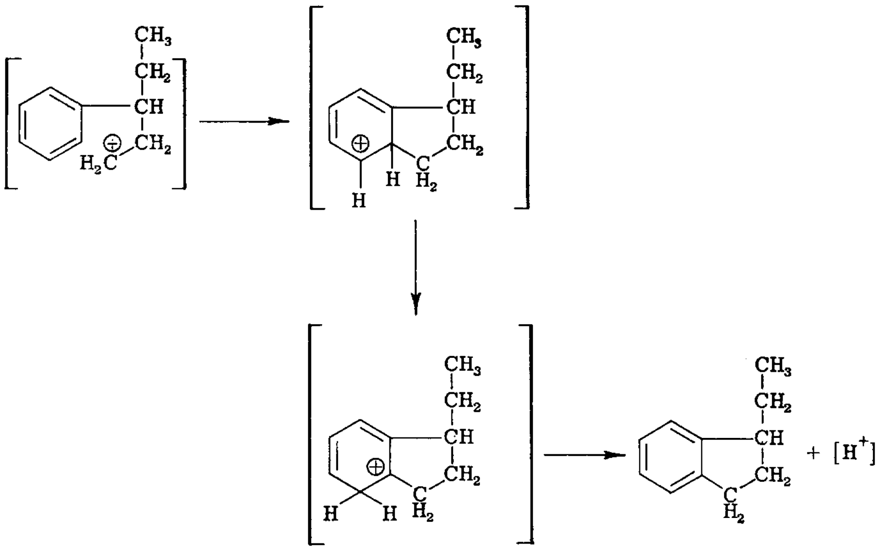
We assume that the remaining two reactions of fragmentation and dehydrocyclization are related to the formation of a carbonium ion with a positive charge in the side chain of 3-phenylpentane



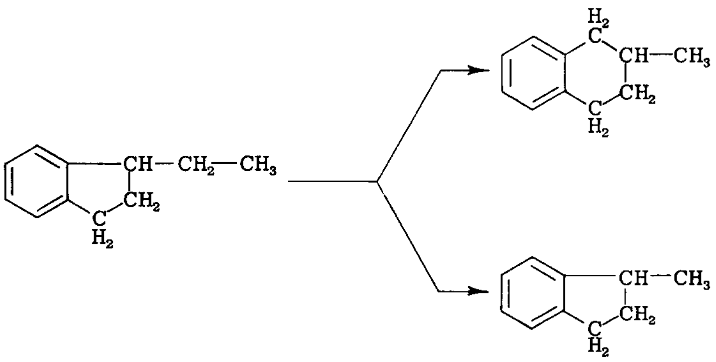
The formation of a positively charged carbonium ion in the ring occurs much more easily than the formation of a carbonium ion with positive charge in the side chain and on that account the basic reaction in the case examined is dealkylation.

The closing of a second ring is possible through the formation of a positively charged carbonium ion at the first carbon atom in the side chain (see top of p. 108).

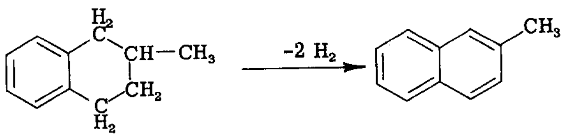
This accounts for the fact that the reaction of dehydrocyclization runs at the relatively lowest degree.



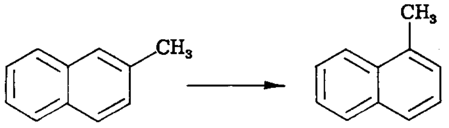
In all probability, the ethylindane obtained during the reaction of dehydrocyclization undergoes isomerization under the conditions of the reaction with expansion of the ring to methyltetralin or is cracked to methylindane



Dehydrogenation of methyltetralin leads to the formation of β-methylnaphthalene



which undergoes partial isomerization to α-methylnaphthalene

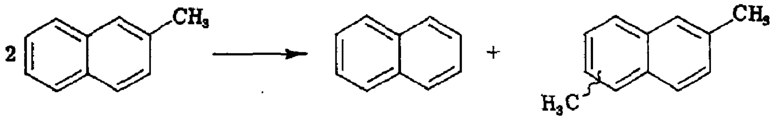


and partial disproportionation to naphthalene and dimethylnaphthalene (next page).

All these reactions, secondary with regard to cyclization, have been observed by other authors in the presence of acid catalysts.

In this manner, it is demonstrated on the basis of the data obtained in the course of the present work that both C_6 and C_5 dehydrocyclization occur on the silica-alumina catalyst.

We are continuing with our investigations on the catalytic conversions of isomeric amylgenzenes in the reaction of



dehydrocyclization on silica-alumina catalysts.

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