

Dehydrocyclization of α -Amylnaphthalene on Silica-Alumina Catalyst

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It has been demonstrated in the course of studying the catalytic conversions of α -*n*-amylnaphthalene on synthetic silica-alumina catalyst that parallel with the reactions of isomerization, fragmentation, and dealkylation there is also a reaction of dehydrocyclization with formation of 2-methylantracene and anthracene. An analogy has been established between the silica-alumina catalyst and the platinum-covered charcoal in the practically selective course of cyclization in the series of monoalkylnaphthalenes to anthracene structures. The assumption is expressed that the above reactions on a silica-alumina catalyst possess an ionic mechanism: the reactions of dealkylation and isomerization are determined by the formation of a carbonium ion with positive charge at the nucleus, the reactions of fragmentation and dehydrocyclization being determined by the formation of a carbonium ion with positive charge at a carbon atom from the side chain.

INTRODUCTION

Some time ago it was reported by Shuikin, Erivanskaya, and Yang-Ai-Hsi (1) that upon passing α -*n*-amylnaphthalene over chromia-alumina catalyst (20% Cr₂O₃) at a temperature of 455–450°C and a space velocity of 0.1 hr⁻¹ they obtained, depending on the activity of the catalyst, from 12.1% to 41.8% of the catalysate weight of naphthalene, from 11.0% to 38.2% of a mixture of α - and β -alkylnaphthalenes whose structures were not determined, and from 33.1% to 36.7% of 1-methylphenanthrene containing only traces of anthracene hydrocarbon. In the same paper the authors refer to the following interesting fact about the selectivity of the chromium-alumina catalyst and platinum-covered charcoal (10% Pt) upon the dehydrocyclization of β -*n*-butylnaphthalene: the sole product of the cyclization during the experiments with platinum-covered charcoal was anthracene, while it was mainly phenanthrene that was obtained during their experiments with chromium-alumina catalyst (2).

It was established in the course of systematic investigations on the catalytic conversions of individual alkylaromatic hydrocarbons of various structures, carried out by one of us and his colleagues (3, 4, 5), that the reaction of dehydrocyclization takes place in the series of mono- and dialkylbenzenes in the presence of a silica-alumina catalyst as well. We found recently that the reaction of dehydrocyclization in the presence of a silica-alumina catalyst is also to be observed in the cracking of α -*n*-butylnaphthalene (6). Upon passing α -*n*-butylnaphthalene at 490°C and a space velocity of 0.88 hr⁻¹ over a synthetic silica-alumina catalyst we obtained 4.6% of the weight of the catalysate of anthracene and traces of phenanthrene discovered by spectral means only. It is obvious that the silica-alumina catalyst also shows a selective action in the closing of a third ring with the participation of the side chain in the series of the monoalkylnaphthalenes.

It was of some interest to check the degree to which the reaction of dehydrocyclization and the selective action of the

silica-aluminas established during its course are of a more general character in the series of the monoalkylnaphthalenes. To this end we studied the catalytic conversions of α -*n*-amylnaphthalene on a silica-alumina catalyst, and the results obtained are presented in this paper.

APPARATUS AND METHODS OF WORK

Along general lines, the apparatus, the amount and composition of the catalyst, and the method of analysis of the products obtained by cracking of α -*n*-amylnaphthalene were analogous to those employed in studying the catalytic conversions of 3-phenylpentane (4).

Nine consecutive experiments were carried out in a glass reactor 20 mm in diameter placed in a furnace with a heat-adjustment device, over 10 ml of synthetic silica-alumina catalyst of the Houdry type, at a temperature of 490°C and space velocity of 0.88 hr⁻¹.

The gaseous products obtained were chromatographically analyzed immediately after the experiment on a stationary phase of dimethylformamide at a temperature of 0°C.

The catalysates of the nine experiments were collected and were subjected to precise rectification on a column with effectiveness of 36 theoretical plates. The narrower fractions obtained were chromatographically and spectrally analyzed. The chromatographic analyses were carried out on the high-temperature device of the Fractovap apparatus, Model B, at a temperature of 250°C, due use being made of the stationary phase SE-30. UV spectra were taken with the Unicam apparatus and infrared spectra with the apparatus UR-10.

For the purpose of identifying the reaction products we used α -ethyl-, α -*n*-propyl-, and α -*n*-butylnaphthalenes synthesized by us, commercial types of naphthalene, α - and β -methylnaphthalenes and anthracene as well as the β -ethyl-, β -*n*-propyl-, β -*n*-butyl-, and β -*n*-amylnaphthalenes and 2-methylantracene which L. A. Erivanskaya was so kind as to place at our disposal.

The synthesis of the initial α -*n*-amyl-

naphthalene was carried out after Würtz-Fittig (7) from α -bromonaphthalene and *n*-amylbromide in the presence of metallic sodium, the yield being 31% of the theoretical. The chromatographically pure alkylnaphthalene obtained in this manner possessed the following constants: b.p. 155–157°C/10 mm; n_D^{20} 1.5716; d_4^{20} 0.9669; picrate (not referred to in the literature), m.p. 64–66°C. Literature data (7): b.p. 164–165°C/19 mm; n_D^{20} 1.5728; d_4^{20} 0.9668.

In order to test the influence of the temperature and of the space velocity on the catalytic conversions of α -*n*-amylnaphthalene, experiments were also carried out at three different temperatures (410°, 450°, and 490°C) and at four different space velocities (0.31, 0.88, 1.34, and 1.77 hr⁻¹). Each one of these experiments lasted 15 min and the catalysates obtained in this instance were analyzed chromatographically only.

RESULTS AND DISCUSSION

The investigations already carried out by us on the catalytic conversions of the individual alkylaromatic hydrocarbons containing four and more carbon atoms in the side chain, showed that the catalytic cracking of these compounds has a rather complex course involving the formation of a large number of hydrocarbons which boil in a broad temperature interval. In order to obtain the fullest possible picture about the number and structure of the cracking products, we carried out several consecutive experiments under identical conditions. Such experiments were also made with α -*n*-amylnaphthalene at a temperature of 490°C and at a space velocity of 0.88 hr⁻¹. As a result of these experiments we obtained gas, liquid catalysate, and coke.

The following components were chromatographically identified in the composition of the gas: hydrogen, methane, ethane, ethylene, propane, propylene, isobutane, *n*-butane, isobutene, *trans*-2-butene, *cis*-2-butene, isopentane, and *n*-pentane. Methane and hydrogen account for 86% of the general composition of the gas.

The liquid catalysate was subjected to

chromatographic analysis and the chromatogram is shown in Fig. 1.

It becomes clear from Fig. 1 that the catalysate obtained during the cracking of α -*n*-amyl-naphthalene consists of eight basic components, which were identified by means of markers as naphthalene (1); methylnaphthalene (2); ethylnaphthalene (3); *n*-propylnaphthalene (4); *n*-butylnaphthalene (5); *n*-amyl-naphthalene (6); anthracene (7); and 2-methylantracene (8).

the catalysate possessed a qualitative composition analogous to the gas collected in the gasometer in the course of the catalytic experiment.

The remaining fractions underwent chromatographic, spectral, and chemical analyses, the results of which are presented in Table 1.

It was proved by using a stationary phase composed of a mixture of lanolin and castor oil in a 4:1 ratio that in fraction No. 3, 56% of the total content of methyl-

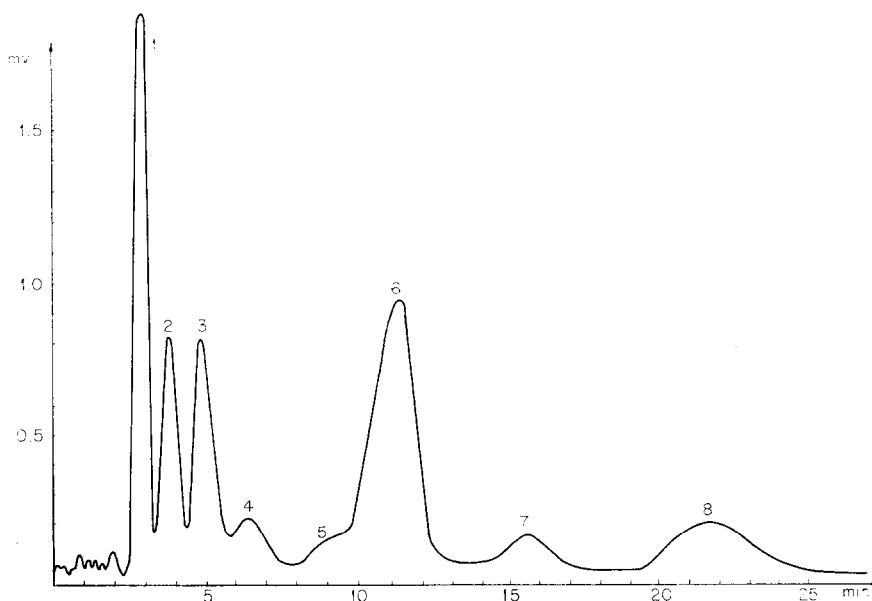


FIG. 1. Chromatogram of catalysate, obtained during the cracking of α -*n*-amyl-naphthalene in the experiments at 490°C and 0.88 hr⁻¹: 1, naphthalene; 2, α - and β -methylnaphthalene; 3, α - and β -ethylnaphthalene; 4, α - and β -*n*-propylnaphthalene; 5, α - and β -*n*-butylnaphthalene; 6, α - and β -*n*-amyl-naphthalene; 7, anthracene; 8, 2-methylantracene.

Since at a temperature of 250°C and upon the utilization of the stationary phase SE-30 the α - and β -isomers on the one hand and the anthracene and phenanthrene on the other do not undergo separation, we subjected the catalysate to precise rectification for the purpose of obtaining fractions enriched in the separate components. The catalysate was in this manner divided into 11 fractions, four of which (Nos. 2, 9, 10, and 11) were solids and one (No. 1) consisted of gaseous products.

The gas obtained upon stabilization of

naphthalene belong to the β -isomer and 44% to the α -isomer.

Infrared spectra were used to prove that the fractions enriched in ethyl-, *n*-propyl-, *n*-butyl-, and *n*-amyl-naphthalenes also consist of α - and β -isomers. In fraction 7, for instance, which is virtually pure *n*-amyl-naphthalene, it is the α -isomer that is predominant, as compared with the predominance of the β -isomer in fraction No. 8 which contains 95% *n*-amyl-naphthalene.

Predominant in the crystallized products of fractions No. 9 and No. 10 are anthra-

cene structures (885 and 895 cm^{-1}). However, they also show bands indicating the presence of phenanthrene (870 cm^{-1} ; 1605–1625 cm^{-1}). After twofold recrystallization from ethyl alcohol, the crystalline product from fraction No. 9 melted at 206–208°C, while that of fraction No. 10 melted at 201–203°C. The data existing in the literature (8) on pure anthracene and 2-methylanthracene are 216° and 207°C, respectively, those on the melting point of phenanthrene and 1-methylphenanthrene being 100° and 123°C. After recrystallization, the characteristic bands for phenanthrene structures disappeared from the in-

also contains products whose structure has not been established.

The products identified testify to the fact that the cracking of α -*n*-amyl-naphthalene is a complex process of parallel and consecutive reactions. The basic ones of these reactions affect the side chain, namely,

- (1) isomerization with shifting of the side chain from α - into β -position,
- (2) fragmentation of the carbon-carbon bonds in the side chain,
- (3) dealkylation, and
- (4) dehydrocyclization with the participation of the side chain.

Unfortunately, the complex composition

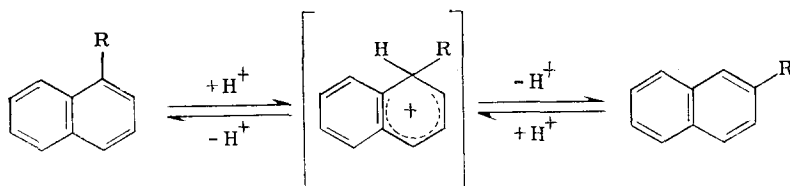
TABLE 1
RESULTS OF THE CHROMATOGRAPHIC ANALYSIS OF THE FRACTIONS OBTAINED UPON THE RECTIFICATION OF THE CATALYSATE FROM THE EXPERIMENTS AT A TEMPERATURE OF 490°C AND A SPACE VELOCITY OF 0.88 HR^{-1}

| Fracton No. | B. p. (°C/760 mm) | Wt. % of catalysate | Cyclic components, in wt. %, of the fraction | | | | | | | |
|--------------------------------|----------------------|------------------------|--|-----------------------------|----------------------------|-----------------------------|----------------------------|----------------------|-----------------|------------------------------|
| | | | Naphtha- lene | Methyl- naphtha- lene | Ethyl- naphtha- lene | Propyl- naphtha- lene | Butyl- naphtha- lene | Amylnaph- thalene | Anthra- cene | 2-Meth- ylanthra- cene |
| 1 | Gas | 2.3 | — | — | — | — | — | — | — | — |
| 2 | 218° | 28.8 | 62.5 | 24.4 | 13.1 | — | — | — | — | — |
| 3 | 218–241° | 5.5 | 17.3 | 52.3 | 30.6 | — | — | — | — | — |
| 4 | 241–256° | 5.7 | — | 13.4 | 86.6 | — | — | — | — | — |
| 5 | 256–272° | 4.0 | — | 0.5 | 41.6 | 52.4 | 5.5 | — | — | — |
| 6 | 272–304° | 6.6 | — | 0.2 | 2.4 | 17.0 | 32.3 | 48.0 | — | — |
| 7 | 304–306° | 20.3 | — | — | — | — | — | 100.0 | — | — |
| 8 | 306–311° | 8.4 | — | — | — | — | — | 93.4 | 6.6 | — |
| 9 | 311–346° | 4.9 | — | — | — | — | — | 16.8 | 40.4 | 42.8 |
| 10 | 346–354° | 7.4 | — | — | — | — | — | — | 11.8 | 88.2 |
| 11 | Residue | 6.1 | — | — | — | — | — | — | 5.5 | 39 |
| | | | <i>Total cyclic products</i> | | | | | | | |
| In wt. % of catalysate | | | 19.9 | 10.4 | 11.6 | 3.2 | 2.3 | 32.1 | 3.7 | 11.0 |
| In wt. % of initial substance | | | 12.6 | 6.6 | 7.3 | 2.0 | 1.5 | 20.3 | 2.3 | 7.0 |
| In moles/100 moles of reactant | | | 19.5 | 9.2 | 9.2 | 2.3 | 1.6 | 20.3 | 2.6 | 7.2 |

frared spectra of the products of fraction No. 9 and fraction No. 10. All this, in addition to the character of the spectra in the ultraviolet region (257 and 297 $\text{m}\mu$), entitle us to maintain that anthracene and 2-methylanthracene are basic products of the cyclization in the particular case examined.

Anthracene and 2-methylanthracene are principal components in the residue from the rectification as well, though this residue

did not enable us to provide precise quantitative data about the reaction of isomerization for the individual monoalkylnaphthalenes. However, the total amount of the β -isomers in the catalysate is over 50%. Among the cracking products of α -*n*-amyl-naphthalene we found none that had the isostructure of the side chain. This gives us grounds to assume that the shifting of the chain from the α - into the β -position runs along an intramolecular mechanism:



The fragmentation of the side chain has a very intense course. From the total amount of products in the catalysate, 27.5% belong to the lower homologues of the α -*n*-amylnaphthalene, 21% belonging to methyl- and ethylnaphthalenes alone. The character of the catalyst and the structure of the products obtained from the fragmentation testify to the fact that the

action of dealkylation, particularly those with four and three carbon atoms in the side chain. The data obtained from the experiments at different temperatures and space velocities (Table 2) are indicative of this. They show that a given temperature the amounts of *n*-butyl-, *n*-propyl-, and ethylnaphthalenes pass through maxima upon changing the space velocity. Of

TABLE 2
COMPOSITION OF THE CATALYSATE, IN WEIGHT PERCENT OF THE INITIAL SUBSTANCE
DEPENDING ON TEMPERATURE AND SPACE VELOCITY

| Temp. (°C/760 mm) | Space velocity (hr ⁻¹) | Catal- ysate yield, wt. % of initial substance | Gas | Naph- thalene | Methyl- naphtha- lene | Ethyl- naph- thalene | Propyl- naph- thalene | Butyl- naph- thalene | Amyl- naphtha- lene | Anthra- cene | 2-Meth- ylan- thracene |
|----------------------|--|--|-----|------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|---------------------------|-----------------|------------------------------|
| 410° | 0.31 | 65 | 1.6 | 13.4 | 5.9 | 3.2 | 0.6 | 1.5 | 31.2 | 1.8 | 5.6 |
| 450° | 0.31 | 62 | 1.6 | 21.4 | 8.7 | 4.0 | 0.6 | 1.2 | 15.8 | 2.3 | 6.5 |
| 490° | 0.31 | 61 | 0.4 | 20.6 | 9.9 | 6.3 | 0.6 | 1.0 | 12.7 | 2.7 | 6.8 |
| 490° | 0.88 | 63.4 | 1.5 | 12.6 | 6.6 | 7.3 | 2.0 | 1.5 | 20.3 | 2.3 | 7.0 |
| 490° | 1.34 | 63.6 | 1.6 | 14.5 | 5.5 | 5.2 | 0.4 | 0.8 | 31.2 | 1.0 | 3.5 |
| 490° | 1.77 | 65.2 | 1.4 | 12.6 | 5.5 | 5.7 | 0.4 | 1.9 | 33.1 | 0.9 | 3.7 |

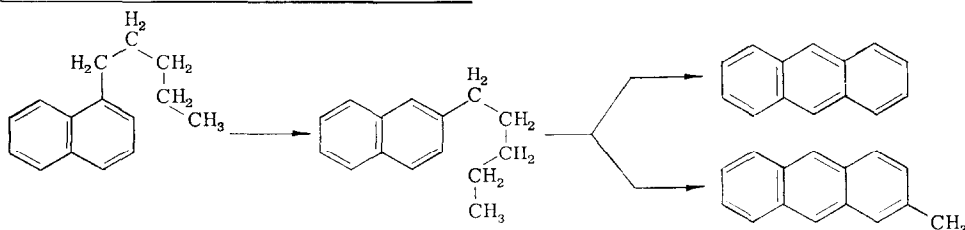
reaction of fragmentation is a typical catalytic cracking of the aliphatic chain.

Unlike what occurs in the cracking of *n*-amylbenzene (β), in the cracking of α -*n*-amylnaphthalene the reaction of dealkylation has a weaker course than the reaction of fragmentation. Of the total amount of the products in the catalysate, 19.9% belong to naphthalene. The latter, however, should not be considered as a product obtained only from the dealkylation of α -*n*-amylnaphthalene. It is highly probable that some of the products of fragmentation may also take part in the re-

course, these products can again take part in the reaction of fragmentation.

In the transition from α -*n*-butyl- to α -*n*-amylnaphthalene there is also a sharp rise in the amount of the dehydrocyclization products—from 4.6% to 14.8% of the weight of the catalysate.

Furthermore, as was the case with the cracking of α -*n*-butylnaphthalene, the cyclization of the α -*n*-amylnaphthalene leads to the formation mainly of anthracene structures. Hence the conclusion that the β -isomer joins the reaction of dehydrocyclization more easily:



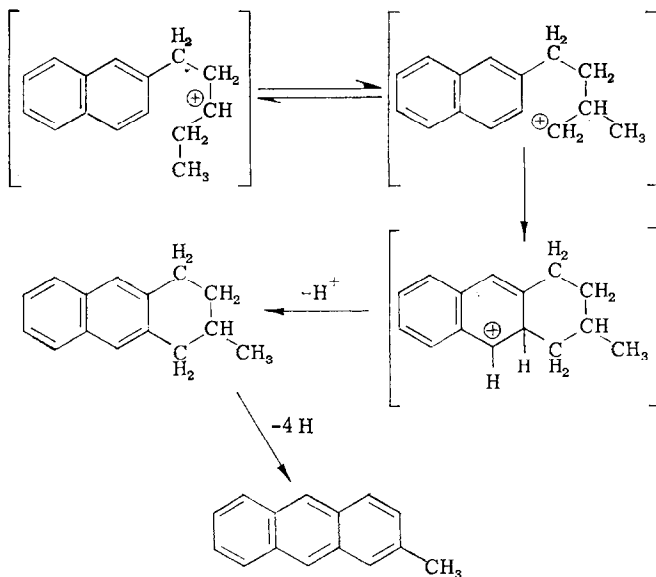
Consequently, there appears a certain analogy in the selective action upon dehydrocyclization in the series of the mono-alkylnaphthalenes between the silica-alumina and the platinum catalysts (2).

As regards the mechanism of dehydrocyclization in the presence of the silica-alumina catalyst, we subscribe to the concept (3, 4) about its ionic character. In our opinion, the velocity of the reactions of dehydrocyclization and fragmentation is to all probability determined by the ease of formation of a carbonium ion with a positive charge at a carbon atom of the side chain:

anthracene, the above diagram is followed in obtaining 1-methylantracene as well. The methyl group in 1-methylantracene breaks off easily, as was shown by Shuikin *et al.* (9). However, anthracene can also be formed through direct cyclization of a fragmentation product.

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The methyltetrahydroanthracene obtained as a result of the dehydrocyclization is dehydrogenated to methylantracene under the conditions of the process. It became clear from our investigations on the cyclization of the isomeric amylbenzenes that a C_5 cyclization runs parallel to the C_8 cyclization. In the case of α -*n*-amyl-naphthalene, however, we did not succeed in discovering in the catalysts the presence of corresponding benzidane structures, despite the fact that their formation is very probable in this case.

Interesting too is the problem related to the manner of anthracene formation. It can be assumed that, parallel with 2-methyl-

REFERENCES

1. SHUIKIN, N. I., ERIVANSKAYA, L. A., AND AI-HSI-YANG, *Zh. Obshch. Khim.* **32**, 823 (1962).
2. SHUIKIN, N. A., ERIVANSKAYA, L. A., AND AI-HSI-YANG, *Dokl. Akad. Nauk SSSR* **133**, 1125 (1960).
3. DIMITROV, CHR., AND PELOVA, R., *Kinetika i Kataliz* **7**, 116 (1966).
4. DIMITROV, CHR., AND IGNATIEV, P., *J. Catalysis* **7**, 103 (1967).
5. DIMITROV, CHR., BESUCHANOVA, C., AND BERDANKOVA, G., *Compt. Rend. Akad. Bulg. Sci.* **19**, 507 (1966).
6. DIMITROV, CHR., AND POPOVA, Z., *Compt. Rend. Akad. Bulg. Sci.* **20**(6), 561 (1967).

7. BAILEY, A. S., PICKERING, G. B., AND SMITH, J. C., *J. Inst. Petrol.* **35**, 103 (1949); *Chem. Abstr.*, p. 6188a (1949).
Publishing Company, Inc., New York, Amsterdam (1946).
8. "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 13, (III), pp. 199, 213, 214. Elsevier
9. SHUIKIN, N. I., ERIVANSKAYA, L. A., KOMISAROVA, N. L., AND AI-HSI-YANG, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, p. 327 (1962).