

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY AT ARMOUR INSTITUTE OF TECHNOLOGY]

Aromatization of *n*-Octane and *n*-Decane in the Presence of Nickel-Alumina Catalyst

By V. I. KOMAREWSKY AND C. H. RIESZ

In a previous article¹ the alkylation of aromatic and naphthenic hydrocarbons with olefin in the presence of nickel-alumina catalyst was described. In the attempt to perform the same reaction with paraffin hydrocarbons it was necessary to study first the behavior of paraffins alone toward the same catalyst. It was found that the paraffin hydrocarbons *n*-octane and *n*-decane undergo dehydrogenation, accompanied by cyclization, the final products being aromatic hydrocarbons. Thus, *n*-octane at 300° yielded a liquid stable toward permanganate. From this liquid, 10% (by weight of *n*-octane charged) of toluene was isolated. The gases from the reaction contained hydrogen and methane (no olefins). These facts show that *n*-octane undergoes dehydrogenation and aromatization to ethylbenzene and the latter decomposes to toluene and methane, as it was shown in another paper.² Similarly *n*-decane at 350° over the same catalyst gave a liquid from which 2% toluene was isolated, together with a higher boiling fraction which was not identified. In the reaction gases hydrogen and methane were found. These facts show that *n*-decane also undergoes dehydrogenation and cyclization with splitting of the aromatic formed to toluene and methane. In addition iso-paraffins (1.6%) were found in the aromatic-free product by the antimony pentachloride method.³

Comparing these results with the work of Kazansky and Plate⁴ and Moldavsky and Kamusher,⁵ a definite difference in the action of nickel-alumina catalyst must be noticed. Thus, the platinum charcoal used by Kazansky and Plate produced from *n*-octane at 300° a mixture of ethylbenzene and *m*-xylene. Chromium oxide catalyst used by Moldavsky and Kamusher produced at 460° the same aromatic hydrocarbons and olefins. Nickel-alumina produced toluene.

Only traces of aromatization were observed with iso-octane and diisoamyl over nickel-alumina

catalyst at 300–350° and, in addition, olefins were formed.

Experimental Part

Apparatus and Procedure.—The paraffin hydrocarbons were passed at the rate of 3–4 cc. per hour through a glass tube of 14 mm. inside diameter filled with 40 g. of 8–10 mesh catalyst. The slow stream of nitrogen simultaneously was passed through the tube. The tube was placed in a horizontal electric furnace. The liquid products were fractionated by a micro-Podbielniak column. The gases were analyzed by the Göckel method.

Material.—*n*-Octane, *n*-decane, and diisoamyl were synthesized by the Wurtz method from *n*-butyl bromide and *n*-amyl bromide, respectively. *n*-Octane, b. p. 124.5–125°, *n*_D²⁰ 1.3950; *n*-decane, b. p. 169–170.5°, *n*_D²⁰ 1.4098, diisoamyl, b. p. 156–158°, *n*_D²⁰ 1.4067. Iso-octane was Röhm and Haas Co. product, b. p. 99–100°, *n*_D²⁰ 1.3866. Nickel-alumina catalyst was prepared according to the procedure of Zelinsky and Komarewsky.⁶

Aromatization

***n*-Octane.**—At 300°, 50.0 g. of *n*-octane yielded 48.5 g. of liquid, *n*_D²⁰ 1.4130, stable toward permanganate. Distillation gave fractions of the following weight, boiling point and refractive index: (1) 5 g., 110–115°, *n*_D²⁰ 1.4750; (2) 2.2 g., 115–123°, *n*_D²⁰ 1.4050; (3) 37.0 g., 123–126°, *n*_D²⁰ 1.3950; (bottoms) 1.0 g., no boiling point, *n*_D²⁰ 1.4120. Nitration of the first fraction gave crystals of 2,4-dinitrotoluene, m. p. 70°.

Anal. Calcd. for C₈H₈·CH₃: C, 91.3; H, 8.7. Found: C, 91.1; H, 8.9.

***n*-Decane.**—At 350°, 39.9 g. of *n*-decane yielded after two passages 25.6 g. of a liquid, *n*_D²⁰ 1.4122, stable toward permanganate. Distillation of 22.9 g. gave fractions of the following weight, boiling point and refractive index: (1) 0.5 g., 105–120°, *n*_D²⁰ 1.4790; (2) 0.5 g., 120–165°, *n*_D²⁰ 1.4150; (3) 2.2 g., 165–169°, *n*_D²⁰ 1.4105; (4) 14.5 g., 169–170.5°, *n*_D²⁰ 1.4108; (5) 3.2 g., 170.5–172°, *n*_D²⁰ 1.4125; (bottoms) 2.0 g., no boiling point, *n*_D²⁰ 1.4590. Nitration of the first fraction gave crystals of 2,4-dinitrotoluene, m. p. 70°. The gas from the reaction contained 25% hydrogen and 75% paraffin (index 1.0). 9.4% of aromatics were found on the total product with fuming sulfuric acid. Distillation of 16.9 g. of the aromatic-free product gave fractions of the following weight, boiling point and refractive index: (1) 3.7 g., 165–169°, *n*_D²⁰ 1.4085; (2) 12.8 g., 169–170.5°, *n*_D²⁰ 1.4098; (bottoms) 0.4 g., no boiling point, *n*_D²⁰ 1.4100. The boiling range of fraction (1) is lower than that of the original material. Since this fraction does not contain any olefins or aromatics, iso-paraffins must be present. By the antimony pentachloride method³ 11.6% of isoparaffins was found in fraction (1).

(6) Zelinsky and Komarewsky, *Ber.*, **57**, 667 (1924).

(1) Komarewsky, *THIS JOURNAL*, **59**, 2715 (1937).

(2) Ipatieff and Komarewsky, *ibid.*, **58**, 922 (1936).

(3) Moldavsky, *Compt. rend. (U. S. S. R.)*, **1**, 507 (1935).

(4) Kazansky and Plate, *Ber.*, **69**, 1862 (1936).

(5) Moldavsky and Kamusher, *Compt. rend. Acad. Sci. U. S. S. R.*, **1**, 9 (1936).

Isooctane produced at 350° a liquid with n^{25}_D 1.3880, traces of reaction with nitrating mixture.

Diisoamyl produced at 300, 325 and 350° a liquid with n^{25}_D 1.4080, 1.4090 and 1.4090, respectively. The combined product contained 9.7% of olefins and traces of aromatics.

Summary

In the presence of nickel-alumina catalyst,

the normal paraffins *n*-octane and *n*-decane undergo dehydrogenation accompanied by cyclization to aromatic hydrocarbons. A splitting forming toluene and methane also takes place which is not observed with catalysts of platinum charcoal or chromium oxide. Isomerization of the normal paraffins also was noted.

CHICAGO, ILLINOIS

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Aromatization of Fatty Alcohols

By V. I. KOMAREWSKY, C. H. RIESZ AND GEORGE THODOS

The role of various substituents of mixed catalysts in heterogeneous catalysis such as promoter and carrier (support) action has assumed prime importance in our present knowledge of the subject. While in many cases it may be difficult to distinguish between catalyst, promoter, and carrier phenomena, the fact remains that only one reaction is catalyzed in one specific direction. There are, however, mixed catalysts which accomplish two or more different reactions, due to the action of each component of the mixed catalyst working in its own specific direction. It is proposed to call such catalysts "complex-action" catalysts.

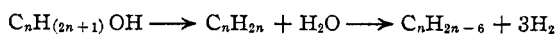
In such cases the resulting reaction is a series of parallel or consecutive steps leading to the formation of desired product.

Thus, by combining nickel oxide and alumina, it was possible to obtain directly from camphor, isocamphane by simultaneous reduction, dehydration and hydrogenation.^{1,2} By combining a polymerizing and hydrogenating catalyst, isooctane was obtained in one step from isobutylene and hydrogen (hydropolymerization).^{3,4} The dehydropolymerization of ethylene⁵ represents another example of these types of reactions.

In the development of these ideas a simultaneous combined reaction of dehydration and dehydrogenation of aliphatic alcohols was carried out. The dehydration of fatty alcohols results in the formation of olefin hydrocarbons which by further dehydrogenation can produce more un-

saturated material such as diolefins and acetylenes. It was of particular interest to perform this type of simultaneous reaction with the fatty alcohols containing a chain of six or more carbon atoms in order to see whether a more complete dehydrogenation of this chain could take place causing cyclization and formation of aromatic hydrocarbons. For these reactions a mixed dehydrating-dehydrocyclizing catalyst was required.

In this work an alumina-chromium oxide catalyst was used; alumina was the dehydrating and chromium oxide the dehydrogenating and cyclizing catalyst. The simultaneous dehydration and dehydrocyclization of *n*-hexyl, *n*-heptyl and *n*-octyl alcohols, and di-*n*-propylcarbinol was performed. As expected it was found that the simultaneous reaction took place with the production of aromatic hydrocarbons according to the scheme



In addition to this reaction, dehydrogenation of the alcohols to aldehydes also took place as shown by the presence of carbon dioxide and carbon monoxide in the reaction gases.

For the fatty alcohols containing six and seven carbon atoms, cyclization of the olefin produced gave the corresponding aromatic hydrocarbon. When *n*-octyl alcohol was subjected to this reaction, a more complex reaction product was obtained. As expected, the eight-carbon chain cyclized to *o*-xylene and ethylbenzene. In addition, however, *m*- and *p*-xylene and toluene were identified. Thus, with this alcohol it is evident that isomerization occurs and *m*- and *p*-xylene are produced by the migration of a methyl

(1) Ipatieff, *Ber.*, **45**, 3205 (1912).

(2) Ipatieff and Matov, *J. Russ. Phys.-Chem. Soc.*, **44**, 1695 (1912).

(3) Ipatieff and Komarewsky, *This Journal*, **59**, 720 (1937).

(4) Ipatieff and Komarewsky, *Ind. Eng. Chem.*, **29**, 958 (1937).

(5) Komarewsky and Balai, *ibid.*, **30**, 1051 (1938).