Chemistry

1958

Abstract

Full Text

Chemistry

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Hydrocarbons of the Decalin Series in Mirzaani Oil

(Presented by Academician B. A. Kazanskii, 24 IV 1958)

A thorough study of the chemical composition of petroleum distillates with boiling points above 150° is one of the current and most important tasks of petroleum chemistry.

We have shown that the 150-200° fraction of Mirzaani oil contains 23.6% hydroaromatic hydrocarbons. It was of interest to establish the individual nature of these hydrocarbons, and the present investigation is devoted to this question. Interest in determining the structure of hydroaromatic hydrocarbons of the decalin series in Mirzaani oil was heightened by the fact that in this same oil, among the condensed aromatic hydrocarbons, we had found naphthalene, α- and β-methylnaphthalene, and 1,6-dimethylnaphthalene.

It was of definite interest to show whether the presence of the condensed aromatic hydrocarbons and their hydrogenated analogues found in earlier investigations ([1,2]) is characteristic only of Surakhany lubricating oil, or whether the same may also characterize other oils.

The investigation carried out showed that condensed aromatic hydrocarbons and their hydrogenated analogues are present in Mirzaani oil.

The accumulation of a large body of experimental material will provide grounds for asserting a possible genetic relationship between condensed aromatic hydrocarbons and their hydrogenated analogues.

As a result of the investigation carried out, we have shown that decalin, α-methyldecalin, and 1,6- and 1,7-dimethyldecalins are present in Mirzaani oil.

The study of naphthenic hydrocarbons in the kerosene of various oils of the Soviet Union, primarily the content in them of decalin and its homologues, is being carried out in the laboratory named after S. S. Nametkin of the Institute of Petroleum of the Academy of Sciences of the USSR.

L. M. Rozenberg ([2]), using dehydrogenation catalysis and the picrate method, investigated hydrocarbons of the decalin series in the kerosene of Surakhany (lubricating) oil and established that it contains decalin, a mixture of α- and β-methyldecalins, and 1,6-dimethyldecalin. L. M. Rozenberg and S. S. Nifontova

([3]), by the same methods, established in the kerosene of Dossor oil the presence of the same hydrocarbons as in the kerosene of Surakhany (lubricating) oil, with the exception of decalin.

The object of investigation in the present work was the 150–200° fraction of an average sample of Mirzaani oil, which was isolated from the oil by fractional distillation.

In order to remove the nonhydrocarbon components included in the 150–200° fraction of Mirzaani oil, it was treated with 75% sulfuric acid, after which it was washed, dried, and distilled from a Favorskii flask in the presence of metallic sodium.

For the investigated fraction 150–200°, the maximum aniline point, refractive index, and specific gravity were determined; their values are given in Table 1.

Table 1

Properties of the 150–200° fraction of Mirzaani crude oil before and after catalysis

	Maximum aniline point before catalysis	Maximum aniline point after catalysis	n_D^{20} before catalysis	n_D^{20} after catalysis	d_4^{20} before catalysis	d_4^{20} after catalysis
Before removal of aromatic hydrocarbons	58.4	46.4	1.4363	1.4432	0.7810	0.7900
After removal of aromatic hydrocarbons	68.4	71.3	1.4210	1.4018	0.7593	0.7514

The separation of the aromatic hydrocarbons included in the investigated fraction was carried out by chromatographic adsorption on KSM-grade silica gel. The working fraction had 100–200 mesh, and its activity with respect to benzene was 13.5.

The completeness of dearomatization was checked according to A. M. Nastyukov (4). For the dearomatized fraction, after the appropriate washing, drying, and distillation, the same physical constants as before removal of the aromatic hydrocarbons were determined; their values are given in Table 1.

To establish the nature of the naphthenic hydrocarbons, the dearomatized gasoline was subjected to dehydrogenation over platinized charcoal (Pt 10%) containing iron, in order to suppress the hydrogenolysis reaction of cyclopentane hydrocarbons, as was shown by B. A. Kazanskii and G. S. Landsberg (5). The dehydrogenating ability of the catalyst was checked according to G. S. Pavlov. The catalyst converted 95% of cyclohexane into benzene.

The aromatic hydrocarbons formed as a result of the dehydrogenation of hydroaromatic hydrocarbons were removed in the same way as the aromatic hydrocarbons of straight-run gasoline. For the catalyzate, before and after removal of the aromatic hydrocarbons, the same constants were determined (Table 1).

From the depression of the aniline points, using the corresponding coefficients, the group composition of the investigated fraction was calculated (height in percent): aromatics 15.1; hydroaromatics 23.6; remaining cyclanes 27.3; paraffins 34.0. The percentage of hydroaromatics relative to the total amount of cyclanes was 46.3.

The aromatic hydrocarbons formed as a result of catalysis were separated by chromatographic adsorption, washed, dried, and distilled from a Favorskii flask in the presence of metallic sodium; the properties and quantity of the collected aromatic-hydrocarbon fractions are given in Table 2.

The fractions of aromatic hydrocarbons, for the purpose of separating condensed aromatic hydrocarbons, were treated separately with picric acid.

From the 135–155° and 155–175° fractions, pure picric acid precipitated. After crystallization, both precipitates had m.p. 122–123° and gave no depression with picric acid, whence it follows that they contained neither naphthalene nor its homologs.

From the 175–195° fraction a picrate was obtained which, after several recrystallizations from ethyl alcohol, gave two picrates: one—needle-shaped—

Table 2

Properties and amounts of the aromatic-hydrocarbon fractions isolated from the catalysate of the 150–200° fraction of Mirzaani oil

Fraction no.	B.p., °C (736 mm Hg)	n_D^{20}	d_4^{20}	Amount of fraction, g
1	135–155	1.4792	0.8321	15
2	155–175	1.4860	0.8421	17
3	175–195	1.4930	0.8643	20

Fraction no.	B.p., °C (736 mm Hg)	n_D^{20}	d_4^{20}	Amount of fraction, g
4	195–220	1.5140	0.9319	20

crystals of orange-yellow color with m.p. 141°, which corresponds to the m.p. of the picrate of α-methylnaphthalene. According to the literature data ([6]), the m.p. of α-methylnaphthalene picrate is 141°. The second—yellow crystals—melts at 149° and corresponds to the m.p. of naphthalene picrate. In the literature, the m.p. of naphthalene picrate is given as 149.5° ([7]).

From the 195–220° fraction a picrate was obtained, from which, after several recrystallizations from ethyl alcohol, two picrates were obtained: one—bright orange in color, with m.p. 111–112°, corresponding according to the literature data to the picrate of 1,6-dimethylnaphthalene ([8]); the second, which melts at 120–121°, corresponding to the picrate of 1,7-dimethylnaphthalene ([8]).

On the basis of the isolated picrates, we have established the presence in Mirzaani oil of decalin, α-methyldecalin, and 1,6- and 1,7-dimethyldecalins.

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Received
24 IV 1958

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Note: Figure translations are in progress. See original paper for figures.