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Note

Gas chromatographic separation and identification of bicyclic aromatic hydrocarbons in kerosene (b.p. 200–280°)

M. C. PANKOVA, R. S. MILINA, R. P. BELCHEVA and A. S. IVANOV

Economic Corporation "Neftochim" Refinery and Petrochemical Developments Institute, Bourgas (Bulgaria)

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The separation and identification of individual bicyclic hydrocarbons in oil fractions (b.p. >200°) is a difficult problem. The usual gas chromatographic techniques are not suitable for the analysis of kerosene (b.p. 200–280°) over such a wide temperature range, because this fraction contains mainly paraffins and naphthenes and about 15–20% of aromatics, of which 3–4% are bicyclics. The naphthalene hydrocarbons consist of many isomers with similar physical and chemical properties, which pose difficulties in their gas chromatographic separation.

The qualitative and quantitative determination of naphthalene hydrocarbons has been studied by a number of workers using chromatographic methods^{1–4} or combinations of gas chromatography with spectral methods^{5–7}. Most of the work involved investigations of artificial mixtures of naphthalene hydrocarbons^{1,2,5,6} with little emphasis on the separation of dimethylnaphthalenes.

In this work, the high-boiling kerosene fraction (b.p. 200–280°) containing mono-, di-, tri- and some tetraalkylnaphthalenes and heteroatomic compounds (mainly sulphur components) has been investigated in order to separate and identify the individual bicyclic hydrocarbons.

EXPERIMENTAL AND RESULTS

We carried out a vacuum distillation of the fraction in a distillation column with 20 theoretical plates and separated five narrow fractions (b.p. 200–240°, 240–250°, 250–260°, 260–270° and 270–280°). Spectrophotometry showed that the proportion of bicyclics in these fractions increased from about 2% bicyclics in the first to about 25% in the last two fractions, *i.e.*, the bicyclic hydrocarbons are concentrated in the latter fractions.

The gas chromatographic separation of bicyclic hydrocarbons from the remainder of the fraction could be achieved by using a selective stationary phase that could separate not only different compounds such as paraffins, naphthenes and aromatics, but also the mono- and bicyclic hydrocarbons. The most suitable stationary phase was polyethylene glycol adipate³.

We carried out a preparative separation of the bicyclic hydrocarbons from the

narrow fractions, followed by separation of the individual bicyclics in order to identify them by measuring their UV spectra. The apparatus and operating conditions were as follows: gas chromatograph, Fractovap 2400 T (Carlo Erba, Milan, Italy); detector, katharometer; column, stainless steel (6 m \times 8 mm I.D.); stationary phase, 15% polyethylene glycol adipate (PEGA) deposited on acid-washed Celite (60–80 mesh) at 180°; injection port temperature, 300°; manifold temperature, 280°; detector temperature, 280°; carrier gas, nitrogen at a flow-rate of 60 ml/min; sample size, 200 μ l.

The fraction of b.p. 200–280° was separated into a paraffin-naphthene part, an unsaturated part and an aromatic part using fluorescent indicator adsorption (FIA). These parts were separated chromatographically under conditions as stated above. The aromatics were treated before and after separating of the bicyclic hydrocarbons by preparative thin-layer chromatography. It was shown that the last hydrocarbon of paraffin-naphthenes, unsaturated compounds and monoaromatics is eluted before naphthalene, which was also confirmed by adding hydrocarbons of b.p. > 300°, which were also eluted before naphthalene.

We separated preparatively two fractions, the first containing only bicyclic hydrocarbons and the second the other hydrocarbons. These fractions were checked on an analytical column (7 m \times 4 mm I.D. with the same stationary phase) and showed a good separation of bicyclics from the other hydrocarbons.

The individual bicyclic hydrocarbons in the "naphthalene" fraction were separated preparatively with greater precision under the same conditions on a 7 m \times 4 mm I.D. column with a sample size of 10 μ l. In this instance we used a flame-ionization detector (FID) and a splitting ratio of 1:30. The components for UV spectrophotometry were collected in *n*-heptane (UV grade) with cooling. For the concentration of individual components in *n*-heptane, 5-fold preparative sampling was sufficient. Under these conditions fractions that contained one or two compounds were collected.

The naphthalene hydrocarbons give spectra with a wide absorbance range (210–330 nm) that contain three marked ranges: a sharp maximum at about 200 nm, a wide band with a poorly expressed vibration structure at 230–290 nm and a range with marked fine structure at 290–330 nm^{8,9}. The last range is the most suitable because this absorption is specific for the naphthalene compounds.

The spectral analysis was carried out with a Unicam SP-700 UV spectrophotometer and the identification of naphthalenes was carried out by using pure substances and reference UV spectra^{8,9}. The UV spectra of the preparatively collected components showed, in some instances, the presence of two compounds in one peak and we achieved complete separations on a capillary column with the same stationary phase in order to observe the elution sequence of these components.

The operating conditions were as follows: detector, FID; column, stainless-steel capillary (100 m \times 0.25 mm I.D.); stationary phase, 9% PEGA in benzene at 180°; injection port temperature, 300°; sample size, 1 μ l; splitting ratio, 1:100; carrier gas, nitrogen at a flow rate of 100 ml/min; hydrogen flow-rate, 30 ml/min; and oxygen flow-rate, 240 ml/min.

We succeeded in identifying 80% of the bicyclic hydrocarbons that were separated on the capillary column. We determined the Kováts retention indices of all of the identified bicyclic hydrocarbons (b.p. 200–280°) and Table I gives their

TABLE I

KOVÁTS RETENTION INDICES OF BICYCLIC AROMATIC HYDROCARBONS IN THE 200–280° KEROSENE FRACTION ON PEGA AT 180°

No.	Compound	Kováts retention index	Identification method
1	Naphthalene	1886.1	Ethalon
2	2-Methylnaphthalene	1969.8	Ethalon and UV spectrum
3	1-Methylnaphthalene	2015.6	Ethalon and UV spectrum
4	2-Ethylnaphthalene	2053.5	Ethalon and UV spectrum
5	1-Ethylnaphthalene	2058.9	Ethalon and UV spectrum
6	1,6-Dimethylnaphthalene	2070.2	UV spectrum
7	2-Ethylnaphthalene	2083.6	UV spectrum
8	Dialkylnaphthalene	2101.2	UV spectrum
9	1,3-Dimethylnaphthalene	2110.8	Ethalon and UV spectrum
10	1- <i>n</i> -Propylnaphthalene	2120.8	UV spectrum
11	1- <i>n</i> -Butylnaphthalene	2130.9	UV spectrum
12	1,4- and 2,3-Dimethylnaphthalene	2139.4	Ethalon and UV spectrum
13	1,5-Dimethylnaphthalene	2145.1	Ethalon and UV spectrum
14	2,6-Dimethylnaphthalene	2158.8	UV spectrum
15	2,7-Dimethylnaphthalene	2169.3	UV spectrum
16	2-Methyl-7-isopropylnaphthalene	2173.9	UV spectrum
17	1,8-Cycloalkenylnaphthalene	2182.6	UV spectrum
18	1,2,7-Trimethylnaphthalene	2192.2	UV spectrum
19	1,4-Dialkylnaphthalene	2204.1	UV spectrum
20	1,3,5-Trimethylnaphthalene	2223.8	UV spectrum
21	2,3-Dihydrophenalene	2231.6	UV spectrum
22	1-Methyl-7-isopropylnaphthalene	2236.5	UV spectrum
23	1,3,6-Trimethylnaphthalene	2248.1	UV spectrum
24	1,6,7-Trimethylnaphthalene	2257.3	UV spectrum
25	1,4,6-Trimethylnaphthalene	2258.1	UV spectrum
26	1,2,4-Trimethylnaphthalene	2273.3	UV spectrum
27	1,2,5-Trimethylnaphthalene	2280.5	UV spectrum
28	Compound of the tetrahydroanthracene type	2292.1	UV spectrum
29	Trialkylnaphthalene	2297.3	UV spectrum
30	1,2,8-Trimethylnaphthalene	2309.5	UV spectrum
31	1-Propyl-2-cyclohexylnaphthalene	2325.6	UV spectrum
32	α,ϵ -Cycloalkylnaphthalene	2330.8	UV spectrum
33	Trialkylnaphthalene	2338.5	UV spectrum
34	1,6-Dimethyl-4-isopropylnaphthalene	2345.2	UV spectrum
35	1,4,5-Trimethylnaphthalene	2388.1	UV spectrum
36	3-Alkylbenzo(<i>b</i>)thiophene	2992.6	UV spectrum
37	2,3,6,7-Tetramethylnaphthalene	2401.3	UV spectrum
38	1,2,3,4-Tetramethylnaphthalene	2409.2	UV spectrum
39	6-Alkylbenzo(<i>b</i>)thiophene	2412.0	UV spectrum
40	1,2-Dimethyl-7-ethylnaphthalene	2417.3	UV spectrum
41	2-Alkenylnaphthalene	2423.8	UV spectrum
42	1,4-Diethyl-6-methylnaphthalene	2425.6	UV spectrum
43	1,6-Diethyl-4-methylnaphthalene	2433.3	UV spectrum
44	2-Alkylnaphthalene	2444.7	UV spectrum
45	1,2,3-Trialkylnaphthalene	2448.6	UV spectrum
46	1,4,6-Trialkylnaphthalene	2480.3	UV spectrum
47	1,2,7-Trialkylnaphthalene	2516.4	UV spectrum

experimental retention indices and the method of identification used. The experimental retention indices were obtained in four replicate experiments and showed good repeatability (0.5–0.6 index unit).

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