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DETERMINATION OF THE BOILING POINTS OF C₁₀ ISOALKANES IN AN *n*-DECANE ISOMERIZATE FROM GAS CHROMATOGRAPHIC RETENTION INDICES

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SUMMARY

Using the equilibrium isomerization of *n*-alkanes in the presence of an aluminium halide, a standard mixture of isoalkanes consisting of a C₅-C₁₀ *n*-decane isomerizate was obtained. This isomerizate was analyzed by gas chromatography in a copper capillary column, 150 m long, filled with BM-4 vacuum oil at 95°C. From the relationship between the retention characteristics and chemical structures, the boiling points of the C₁₀ isoalkanes were determined directly from artificial mixtures of isomers. Calculations were carried out by using corrected boiling point indices according to Matukuma.

INTRODUCTION

In gas chromatography, the retention values are determined by the nature of the intermolecular interactions between an analyzed compound and the stationary phase. With alkanes, the order of retention times corresponds to that of their boiling points, as the polarity of the stationary phase has only a minor effect on retention time.

To clarify the relationship between the boiling points and retention values, Matukuma¹ proposed the concept of the boiling point index, I_B . He also discussed the relationship between I_B and the Kováts' retention index², I_R . I_B is calculated from the equation

$$I_B = 10^{(0.00134052T_b + 2.558916)} - 440.5 \quad (1)$$

where T_b is the boiling point in °K at 760 mmHg.

Squalane and BM-4 vacuum oil were tested as stationary phases. Although squalane is frequently used as a completely non-polar stationary phase, it is itself polar from the point of view of ideal polarity, as shown by Sidorov and Ivanova³. BM-4 vacuum oil appears to be similar to squalane in its separating properties, although it surpasses it as smaller retention volumes are obtained, thus permitting considerably shorter analysis times and lower pressures at the column inlet.

EXPERIMENTAL AND RESULTS

The synthesis of individual hydrocarbons with a purity that is adequate to determine their boiling points presents certain difficulties. Gas chromatography permits the determination of boiling points directly on a commercial mixture of isomers. For example, Soják and coworkers^{4,5} determined the boiling points of 14 nonenes and decenes and also C₁₂ *n*-alkenes were determined from their gas chromatographic retention indices.

In the present work, we investigated the determination of the boiling points of C₁₀ isoalkanes in a standard mixture of C₅–C₁₀ isomers, obtained by the equilibrium isomerization of alkanes in the presence of an aluminium halide⁶.

n-Decane was isomerized at 300°K in the liquid phase using 10–20% (w/w) of aluminium bromide, the isomerization time being 3–12 h. The catalyst was decomposed by an alkaline solution, and the composition of the reaction products was analysed by gas chromatography. Considerable cracking of highly branched alkanes was observed during prolonged contact with large amounts of catalyst.

The product of *n*-decane isomerization was analyzed on a TSVET-I chromatograph equipped with a capillary column and a flame ionization detector. A copper column, 150 m × 0.25 mm I.D., was used for the separation. The column was filled with vacuum oil by the dynamic method. Measurements were made at 95°C, a carrier gas (nitrogen) pressure of 2.0 kg/cm² and a carrier gas velocity of 1.2 ml/min. The amount of sample fed in was a maximum of 1 ml, and the splitting ratio was 1:300.

A chromatogram obtained is shown in Fig. 1.

The components of the isomerizate of *n*-decane were identified by comparison with certain individual hydrocarbons available to the authors. Hydrocarbons that were lacking were prepared by using the Wurtz reaction and methylene insertion⁷. Isomerizates of *n*-octane, isooctane, and *n*-nonane were also used, as well as some data given by Martynov and Vidergauz⁸.

The reproducibility of the relative retention times was lower than that attainable with modern highly efficient capillary columns. The use of standard calibration mixtures for identification using data from the literature on the relative retention times of corresponding isomeric hydrocarbons makes it possible to exclude this type of error, as the coincidence of relative retention times of certain hydrocarbon series cannot be random in nature.

The retention times of the C₉ and C₁₀ alkanes in the *n*-decane isomerizate were determined relative to *n*-pentane and the results were expressed as Kováts retention indices:

$$I_R = 100 \left(\frac{\log V_x - \log V_{n(z)}}{\log V_{n(z+1)} - \log V_{n(z)}} \right) + 100z \quad (1)$$

where V_x , $V_{n(z)}$, $V_{n(z+1)}$ are corrected retention values for the hydrocarbon measure, an *n*-alkane with z carbon atoms and one with $z+1$ carbons, respectively.

In Table I, the C₉ and C₁₀ alkanes in the *n*-decane isomerizate are listed in order of increasing boiling points. Also given are the I_B and I_R values found experimentally at 95°C.

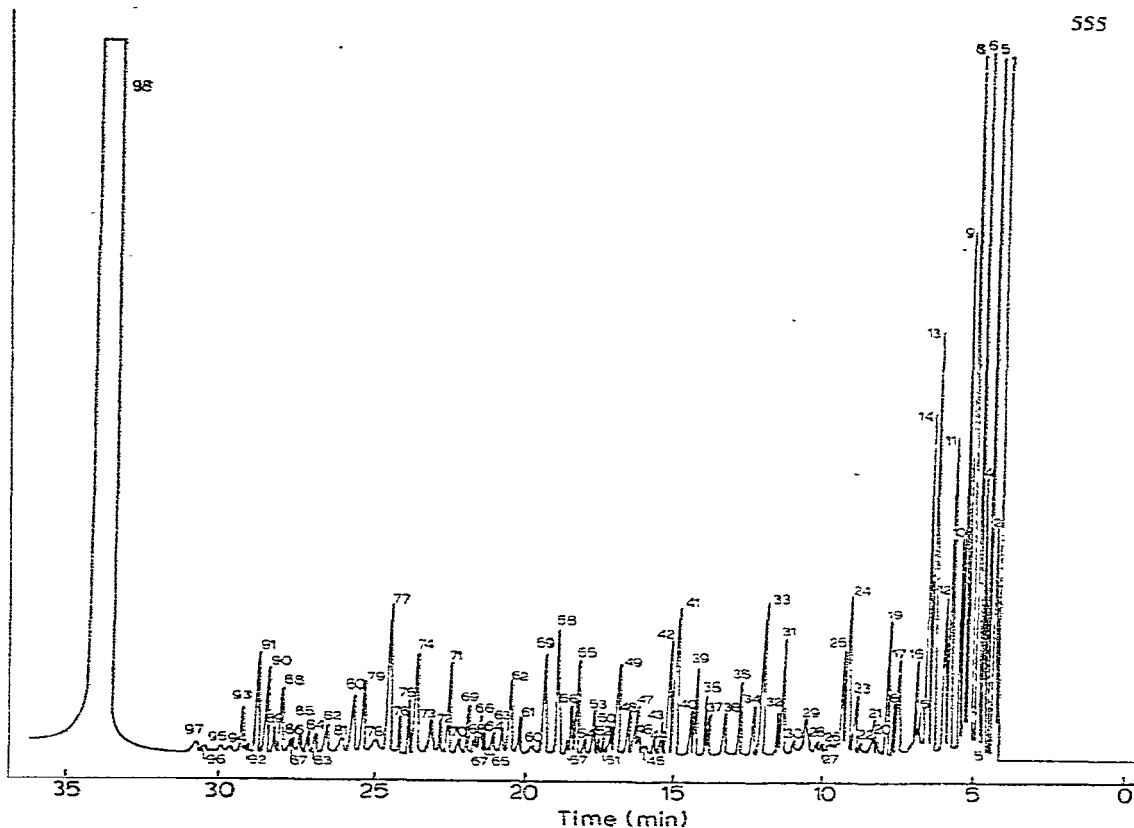


Fig. 1. Chromatogram of *n*-decane isomerizate on BM-4 vacuum oil as stationary phase. Column length, 150 m; column temperature, 95°C. Peaks: 1 = methane; 2 = ethane; 3 = propane; 4 = 2-methylpropane; 5 = *n*-butane; 6 = 2-methylpentane; 7 = *n*-pentane; 8 = 2,2-dimethylbutane; 9 = 2,3-dimethylbutane + 2-methylpentane; 10 = 3-methylpentane; 11 = *n*-hexane; 12 = 2,2-dimethylpentane; 13 = 2,4-dimethylpentane; 14 = 2,2,3-trimethylbutane; 16 = 3,3-dimethylpentane; 17 = 2-methylhexane; 18 = 2,3-dimethylpentane; 19 = 3-methylhexane; 20 = 3-ethylpentane; 21 = *n*-heptane; 23 = 2,2-dimethylhexane; 24 = 2,5-dimethylhexane; 25 = 2,4-dimethylhexane; 26 = 2,2,3,3-tetramethylbutane; 27 = 2,2,3-trimethylpentane; 28 = 3,3-dimethylhexane; 29 = 2,3,4-trimethylpentane; 31 = 2,3-dimethylhexane + 2-methylheptane; 32 = 4-methylheptane; 33 = 2,3,3-trimethylpentane + 3-methylheptane; 34 = 2,2,5-trimethylhexane; 35 = 2,2,4-trimethylhexane; 36 = *n*-octane; 37 = 2,3,5-trimethylhexane; 38 = 2,2-dimethylheptane; 39 = 2,4-dimethylheptane; 40 = 2,2,3-trimethylhexane; 41 = 2,6-dimethylheptane; 42 = 2,5-dimethylheptane; 43 = 3,5-dimethylheptane (α) + 3,5-dimethylheptane (β); 44 = 3,3-dimethylheptane; 45 = 2,3,3-trimethylhexane; 46 = 3,3,4-trimethylhexane; 47 = 2,3-dimethylheptane; 48 = 3-methyl-3-ethylhexane; 49 = 4-ethylheptane + 3,4-dimethylheptane (α); 50 = 3,4-dimethylheptane (β); 51 = 2,3,4-tetramethylpentane; 52 = 4-methyloctane; 53 = 2-methyloctane; 54 = 3-ethylheptane; 56 = 2,6-trimethylheptane; 57 = 3-methyloctane; 58 = 2,2,4,5-tetramethylpentane; 59 = 2,2,4-trimethylheptane; 60 = 2,2,5-trimethylheptane; 61 = 3,3-diethylpentane; 62 = 2,2,4,4-tetramethylhexane; 63 = 2,4,4-trimethylheptane; 64 = *n*-nonane; 65 = 2,2,3,4-tetramethylhexane (α); 69 = 4-propylheptane + 2-methyl-4-ethylheptane + 3,3,5-trimethylheptane; 71 = 2,3,5-trimethylheptane (α) + 2,5-trimethylheptane (β); 72 = 2,4-dimethyloctane; 73 = 4-isopropylheptane; 74 = 2,7-dimethyloctane + 3,6-dimethyloctane (α) + 3,6-dimethyloctane (β); 75 = 2,6-dimethyloctane; 76 = 2,3,3-trimethylheptane + 2,3,4-trimethylheptane (α) + 2,3,4-trimethylheptane (β); 77 = 2,3,4,4-tetramethylhexane + 3,3,4-trimethylheptane + 3,4-dimethyloctane (α + β); 79 = 4,5-dimethyloctane (α) + 4,5-dimethyloctane (β); 80 = 3,4,5-trimethylheptane (α) + 3,4,5-trimethylheptane (β); 82 = 2,2-dimethyl-3-ethylhexane; 84 = 4-ethyloctane; 85 = 2,3-dimethyloctane; 86 = 3-methyl-3-ethylheptane; 87 = 2,2,3,3,4-pentamethylpentane; 88 = 3,3-diethylhexane; 89 = 5-methylnonane; 90 = 4-ethylnonane; 91 = 2-methylnonane + 3-ethyloctane; 92 = 3,4-dimethyl-3-ethylhexane; 93 = 2,3-trimethyl-3-ethylpentane; 95 = 3-methylnonane; 98 = *n*-decane. Peaks 15, 22, 30, 55, 66, 67, 70, 78, 81, 83, 94, 96, 97 are unidentified components.

TABLE I

BOILING POINTS (T_B), BOILING POINT INDICES (I_B) AND RETENTION INDICES (I_R) OF C_5 - C_{10} ALKANES IN n -DECANE ISOMERIZATE ON VACUUM OIL AT 95°C

Hydrocarbon	T_B		I_B		I_R
	Ref. 1	According to eqn. 1	Ref. 1	Experimental	
2,2,5-Trimethylhexane	124.084	124.12	796.4	796.6	774.9
2,2,4-Trimethylhexane	126.54	126.48	802.9	802.72	788.8
2,3,5-Trimethylhexane	131.34	131.3	821.6	821.4	811.7
2,2-Dimethylheptane	132.69	132.54	826.9	826.5	814.2
2,4-Dimethylheptane	132.89	132.8	827.7	827.3	822.1
2,2,3-Trimethylhexane	133.60	133.78	830.5	830.9	824.2
2,6-Dimethylheptane	135.21	135.25	836.8	836.4	826.8
2,5-Dimethylheptane	136.0	136.08	840.0	839.5	832.8
α - + β -3,5-Dimethylheptane	136.0	136.08	840.0	839.5	834.1
3,3-Dimethylheptane	137.01	137.1	843.9	844.1	836.5
2,3,3-Trimethylhexane	137.68	137.65	846.6	846.6	840.7
3,3,4-Trimethylhexane	140.46	140.36	857.7	857.06	854.4
3-Methyl-3-ethylhexane	140.6	140.6	858.2	858.2	855.5
α -3,4-Dimethylheptane	140.6	140.6	858.2	858.2	857.6
β -3,4-Dimethylheptane	140.6	140.6	858.2	858.2	859.8
2,3-Dimethylheptane	140.65	140.72	858.4	859.3	854.8
4-Ethylheptane	141.2	141.31	850.3	861.3	857.6
2,3,3,4-Tetramethylpentane	141.511	141.6	861.9	862.5	860.9
4-Methyloctane	142.42	142.54	865.5	864.9	863.1
3-Ethylheptane	143.0	143.1	867.9	868.5	867.1
2-Methyloctane	143.26	143.4	868.9	869.7	864.3
3-Methyloctane	144.21	144.26	872.8	872.5	871.1
3,3-Diethylpentane	146.168	145.92	880.7	879.6	885.8
n -Nonane	150.798	150.8	900	900	900
2,4,6-Trimethylheptane	147.6	147.42	886.6	885.5	869.8
2,2,4,5-Tetramethylpentane	147.88	174.8	887.7	887.3	873.1
2,2,4-Trimethylheptane	148.3	148.54	889.5	890.2	875.3
2,2,5-Trimethylheptane	150.8	150.96	899.8	900.7	877.6
2,4,4-Trimethylheptane	151.0	151.13	901.0	901.5	892.2
2,2,4,4-Tetramethylhexane	153.8	153.3	912.2	910.5	888.8
3,3,5-Trimethylheptane	155.68	155.54	920.1	917.9	907.7
2,4-Dimethyloctane	155.9	155.95	921.0	920.7	915.5
2-Methyl-4-ethylheptane	156.2	156.63	922.3	924.3	907.7
4-Propylheptane	157.5	157.8	927.8	928.6	907.7
2,6-Dimethyloctane	158.4	158.2	932.2	930.4	930.8
α -2,2,3,4-Tetramethylhexane	158.8	158.68	933.3	932.2	902.8
4-Isopropylheptane	158.9	159.12	933.7	934.5	922.2
2,7-Dimethyloctane	159.87	159.72	937.8	936.3	927.8
α -2,3,4-Trimethylheptane	159.9	160.1	937.9	937.9	933.7
β -2,3,4-Trimethylheptane	159.9	160.1	937.9	938.5	933.7
2,3,3-Trimethylheptane	160.2	160.33	939.3	939.2	933.7
α -2,3,5-Trimethylheptane	160.7	160.5	941.4	940.7	912.3
β -2,3,5-Trimethylheptane	160.7	160.5	941.4	940.7	912.3
α -3,6-Dimethyloctane	160.8	161.2	941.8	943.5	927.8
β -3,6-Dimethyloctane	160.8	161.2	941.8	943.5	927.8
2,3,4,4-Tetramethylhexane	161.6	161.7	945.2	946.3	936.3
3,3,4-Trimethylheptane	161.9	161.7	946.5	946.3	936.3
3,4-Dimethyl-3-ethylhexane	162.1	162.05	947.3	948.5	965.2

TABLE I (continued)

Hydrocarbon	T_B		I_B		I_R
	Ref. 1	According to eqn. 1	Ref. 1	Experimental	
c 4,5-Dimethyloctane	162.13	162.23	947.5	948.7	942.8
f 4,5-Dimethyloctane	162.13	162.23	947.5	948.7	942.8
c 3,4,5-Trimethylheptane	162.5	162.72	949.1	950.3	945.2
f 3,4,5-Trimethylheptane	162.5	162.72	949.1	950.3	945.2
c 3,4-Dimethyloctane	163.4	163.13	952.9	951.2	936.3
f 3,4-Dimethyloctane	163.4	163.13	952.9	951.2	936.3
c Ethyloctane	163.64	163.5	953.9	953.5	950.9
3 Methyl-3-ethylheptane	163.8	163.84	954.6	954.5	952.6
2,3-Dimethyl-3-ethylhexane	163.9	164	955.1	955.5	948.7
2,3-Dimethyloctane	164.31	164.51	956.8	957.5	951.8
5-Methylnonane	165.1	164.92	960.2	960.5	958.6
4-Methylnonane	165.7	165.87	962.8	963.5	960.8
2,2,3,3,4-Pentamethylpentane	166.05	166.0	964.4	964.5	953.1
3,3-Diethylhexane	166.3	166.13	965.5	963.8	957.2
3-Ethyloctane	166.5	166.75	966.3	967.5	964.7
2-Methylnonane	167.0	166.75	963.9	967.5	964.7
3-Methylnonane	167.6	168.0	972.0	971.7	970.2
2,2,3-Trimethyl-3-ethylpentane	169.5	168.9	979.4	977.9	967.3
n-Decane	174.123	174.11	999.8	999.5	1000

Column T_B in Table I gives the boiling points at 760 mmHg calculated directly from the retention times on BM-4 vacuum oil using eqns. 1-4.

$$I_B = I_R \dots\dots (3)$$

$$T_b = T_B + 273.15 \dots\dots (4)$$

In order to solve the problem of correcting the boiling points of some multi-branched alkanes, Matukuma¹ introduced the concept of precursor substances. One can accept that $I_R - I_B = \Delta I_{R-B}$ for every precursor substance, and I_R for the alkane under study is I_B .

For instance, for 3-methyl-3-ethylheptane (3M3EC₇) in the isomerizate obtained, only one precursor exists, viz. 3-methyl-3-ethylhexane (3M3EC₆). Using the I_R for 3M3EC₆, I_B for 3M3EC₇ can be calculated in the following way:

$$I_B(3M3EC_7) = I_B(3M3EC_6) + [I_B(3MC_9) - I_B(3MC_8)] = 858.2 + 99.2 = 957.4$$

T_B for 3M3EC₇ calculated from the value $I_B = 957.4$ can be corrected to a lower temperature

$$I_R(3M3EC_7) - \Delta I_{R-B}(3M3EC_6) = 952.6 + 1.8 = 954.4$$

$$T_B = 163.84$$

For alkanes, the accuracy of the boiling point corrections is about 1°C. How-

ever, for such highly branched hydrocarbons as 3,4M₂3EC₆ and 2,3,5M₃C₆ (α, β), the difference ΔI_{R-B} is considerably higher and T_B must be corrected to a higher temperature than 162.1°C.

For example:

$$(1) I_R(3,4M_23EC_6) - \Delta I_{R-B}(3M3EC_6) = 965.2 + 3.2 = 968.2 \\ T_b = 167.08$$

$$(2) I_R(3,4M_2EC_6) - \Delta I_{R-B}(3,3,4M_3C_6) = 965.2 + 2.6 = 967.8 \\ T_B = 166.75$$

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