DETERMINATION OF THE BOILING POINTS OF STRAIGHT-CHAIN C_{12}-ALKENES FROM THEIR GAS CHROMATOGRAPHIC RETENTION INDICES*

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SUMMARY

The boiling points of all the eleven straight-chain dodecenes were calculated from the retention indices measured for the individual *n*-dodecenes. These indices were determined directly from a technical mixture of *n*-dodecenes obtained by the catalytic dehydrogenation of *n*-dodecane.

A method based on the constants of the proportionality between boiling points and retention indices, as well as the dependence of the above constants on the number of carbon atoms, on the structure of the isomers under comparison, and on the column temperature, was employed for the calculation. The reproducibility of the boiling points calculated from different reference isomers or column temperatures was within ± 0.1°.

The calculated boiling points of the *n*-dodecenes were compared with those from a method of calculation depending on the boiling points of *n*-alkanes between which the *n*-alkene is eluted (maximum deviation −1.9 °) as well as from a calculation according to the corrected index boiling points (maximum deviation −0.4 °).

INTRODUCTION

The catalytic dehydrogenation of higher alkanes produces all the straight-chain alkenes theoretically possible corresponding to the number of carbon atoms in the *n*-alkane. These olefins are important starting materials, for example, in the production of detergents amenable to biodegradation, synthetic alcohols, polymers and copolymers, etc. The identification of the individual products of the dehydrogenation will indicate, on the one hand, the possibility of their isolation and, on the other hand, the possibility of their study from the viewpoint of further reactions. Boiling points or vapour pressures are parameters which represent a

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* Dedicated to Professor Dr. SAMO STANKOVIANSKÝ on the occasion of his 65th birthday.

basic characteristic of substances, and the values of the former are necessary for various calculations.

We have shown recently[1-4] that the individual analysis of the higher straight-chain C_6–C_{12} alkenes is feasible by gas chromatography (GC) on squalane when a high separation-efficiency capillary column is used. The boiling points of all the fourteen nonenes and decenes were obtained from the retention indices measured for the *n*-alkenes. The boiling points of the *n*-undecenes have been published by ASINGER *et al.*[5]. In the case of the *n*-dodecenes, from among the eleven possible isomers, the boiling point of 1-dodecene (213.353 °) and an approximate boiling point of 6-dodecene (213.7 °) are quoted in the literature[6].

In the present paper, we have determined the boiling points of all the straight-chain dodecenes by virtue of the correlation of the retention indices and boiling points of the C_6–C_{12} *n*-alkenes.

EXPERIMENTAL

The measurements were carried out on a Chrom 3 gas chromatograph (Laboratory Instruments, N. E., Prague) with a flame ionization detector. A 200-m long stainless-steel capillary column of 0.2-mm I.D., coated with squalane, was employed. The operation temperatures of the column were 86 °, 100 °, and 115 °. The inlet pressure of the carrier gas (N_2) was 4.0 kg/cm^2, and the carrier gas flow-rate was 1.2 ml/min (at a column temperature of 86 °). The sample size amounted to 0.3–1 μl, at a split ratio of 1:300.

The boiling points of the *n*-dodecenes were calculated from the values determined from the chromatograms of the *n*-dodecane-dehydrogenation products. The retention times of the *n*-dodecenes were measured relative to the retention time of methane, and the data were expressed in the form of Kováts retention indices. The reproducibility of the measurement of the retention indices, from at least three measurements at each temperature, was ± 0.1 index unit. At 86 °, an efficiency of about 300,000 theoretical plates was found. This high efficiency made it possible to resolve isomeric alkenes differing in their boiling points by only 0.1 °. The calculations were carried out on an IBM 360/30 computer in the Research Institute of the Economics of Chemical Industry in Bratislava.

RESULTS AND DISCUSSION

The preparation of the individual *n*-dodecenes of a purity sufficient for the determination of their boiling points is laborious. GC permits the boiling points to be determined directly from a technical mixture of the isomers.

We have hinted at the fact[4] that the precision of the boiling points of structurally similar hydrocarbons, calculated from a relationship based on the linear dependence of the logarithm of absolute or relative retention characteristics on the boiling points of the solutes[7,8], is limited by ignoring the dependence of the vapour pressure and the activity coefficients on the temperature. These dependences markedly manifest themselves mainly in the separation of the *cis–trans* isomers of some *n*-alkenes in such a manner that an inverse sequence of elution was obtained within markedly narrow temperature limits (30 °) in their separation on a non-selective (squalane) liquid phase.

More precise boiling points (reproducibility of ± 0.1 °) have been obtained by us[4] from the correlation of the structure of the individual types of *n*-alkene (such as *trans*-2-, *cis*-2-, *trans*-3-, . . . alkenes) with their retention indices, by virtue of the dependence of the proportionality constant k_p on the number of carbon atoms in the molecule of the *n*-alkene[4].

As the results thus obtained for the C_6–C_{12} *n*-alkenes bear an interesting correlation to those from methods of calculation by means of the boiling points of the *n*-alkanes as well as to the corrected index boiling points[9], results obtained by all the three methods are compared in the present work.

Calculation by use of the proportionality constant k_p

The proportionality constant k_p (ref. 4) characterizes a difference between the retention indices of two isomers, δI, when the difference between their boiling points, δT_b, is 1 °:

$$k_p^{1} = \delta I/\delta T_b \qquad (1)$$

We have found that the proportionality constant k_p of the boiling points and retention indices for C_6–C_{11} *n*-alkenes is dependent on the structure of the pairs of isomers compared, the number of the carbon atoms in their molecules, and the column temperature. Irregular values of k_p were found when comparing isomers with very close boiling points.

The above dependence of the values of k_p on the number of carbon atoms was confirmed for all the temperatures studied (86 °, 100 °, and 115 °). From the regularity of these dependences, the values of k_p were extrapolated for the corresponding pairs of dodecenes (Table I).

TABLE I

EXTRAPOLATED VALUES OF THE PROPORTIONALITY CONSTANT k_p FOR CORRELATED PAIRS OF *n*-DODECENES

Pairs of n-dodecenes under comparison	*Column temperature (°C)*		
	86	*100*	*115*
trans-2/1-alkene	6.3	6.2	6.0
trans-3/1-alkene	4.3	3.9	3.7
cis-2/1-alkene	5.9	5.9	6.0
cis-3/1-alkene	3.3	4.0	4.6
cis-2/*cis*-4	6.5	6.2	6.3
trans-2/*trans*-4	7.8	7.7	7.7
trans-2/*trans*-3	6.9	7.0	6.9
cis-2/*cis*-3	6.4	6.4	6.3
cis-2/*trans*-2	4.3	4.8	5.3
trans-2/*trans*-5	8.0	—	—
cis-2/*cis*-5	6.7	—	—
cis-2/*trans*-4	6.5	—	—
trans-2/*cis*-4	7.2	—	—
trans-2/*cis*-3	7.5	—	—
cis-2/*trans*-3	5.9	—	—

The boiling points of the *n*-dodecenes were then calculated from eqn. 1 arranged in the form:

$$T_{bx} = T_b + (\delta I/k_p) \qquad (2)$$

where T_b is the boiling point of the reference *n*-dodecene.

In this case the fact that the precise boiling point of *n*-dodecene-1 was known was utilized, and this substance served as a reference alkene. First, the boiling points were calculated for those isomers of *n*-dodecenes whose homologues displayed regular dependences of k_p on the number of carbon atoms for the reference 1-alkenes within the range of C_6–C_{11} *n*-alkenes. In this way the boiling points of *trans*-2-dodecene, *trans*-3-dodecene, *cis*-2-dodecene, and *cis*-3-dodecene were calculated. The boiling points of further *n*-dodecenes were calculated by employing as reference alkenes those whose boiling points had already been calculated (*trans*-2-, *trans*-3-, . . . dodecenes). The boiling points of *trans*-6- and *cis*-6-dodecenes were calculated by virtue of their retention indices, carrying out the extrapolation from the boiling points and retention indices of those closest to them, *viz.*, *trans*-5- and *cis*-5-dodecenes; the corresponding isomers have very close temperature increments in the retention indices.

The reproducibility of the boiling points of the individual *n*-dodecenes calculated from different reference isomers or column temperatures was ± 0.1 °. The average values of the boiling points of *n*-dodecenes calculated by means of eqn. 2 are quoted in Table II.

Calculation by use of the boiling points of n-alkanes

By virtue of the rule of similarity of triangles, the following relation was derived for the boiling point, T_{bx}, of a *n*-alkene, eluted between two *n*-alkanes with boiling points T_{b1} and T_{b2} and differing from each other by one carbon atom:

$$T_{bx} = T_{b1} + [\delta I(T_{b2} - T_{b1})/100] \qquad (3)$$

TABLE II

COMPARISON OF BOILING POINTS (°C) CALCULATED BY MEANS OF THE PROPORTIONALITY CONSTANT k_p(A), BY MEANS OF THE BOILING POINTS OF *n*-ALKANES (B), AND FROM THE CORRECTED INDEX BOILING POINTS AFTER MATUKUMA (C)

Method A corresponds with eqn. 2, B with eqn. 3, and C with eqn. 5.

n-Dodecene	*A*	*B*	*ΔT_b (B–A)*	*C*	*ΔT_b (C–A)*
cis-6-Dodecene	212.6	210.8	−1.9	212.2	−0.4
cis-5-Dodecene	212.7	211.0	−1.7	212.3	−0.4
cis-4-Dodecene	213.1	211.7	−1.4	212.7	−0.4
1-Dodecene	213.4	212.6	−0.8	213.3	−0.1
trans-6-Dodecene	213.3	211.9	−1.4	213.2	−0.1
trans-5-Dodecene	213.4	212.1	−1.3	213.3	−0.1
trans-4-Dodecene	213.5	212.4	−1.1	213.4	−0.1
trans-3-Dodecene	214.0	213.2	−0.8	214.0	0.0
cis-3-Dodecene	213.9	212.8	−1.1	213.6	−0.3
trans-2-Dodecene	215.6	215.6	0.0	215.6	0.0
cis-2-Dodecene	216.6	216.3	−0.3	216.4	−0.2

where δI is the difference between the retention index of the n-alkene and that of the n-alkane with the boiling point T_{b_1}.

The boiling points calculated according to eqn. 3 are also listed in Table II. It can be seen from a comparison of the boiling points calculated from eqns. 2 and 3 that the boiling points calculated by eqn. 3 can differ by as much as −1.9°.

TABLE III

VALUES OF DIFFERENCES (ΔT_b) IN BOILING POINTS CALCULATED BY EQNS. 3 AND 2 FOR C_6–C_{12} n-ALKENES

trans-Alkenes	ΔT_b	*cis-Alkanes*	ΔT_b	*1-Alkenes*	ΔT_b
trans-2-Hexene	−0.2	*cis*-2-hexene	1.4	1-hexene	−0.2
trans-2-Heptene	0.1	*cis*-2-heptene	1.2	1-heptene	−0.3
trans-2-Octene	0.0	*cis*-2-octene	0.8	1-octene	−0.4
trans-2-Nonene	0.0	*cis*-2-nonene	0.5	1-nonene	−0.5
trans-2-Decene	0.0	*cis*-2-decene	0.2	1-decene	−0.6
trans-2-Undecene	0.0	*cis*-2-undecene	0.0	1-undecene	−0.7
trans-2-Dodecene	0.0	*cis*-2-dodecene	−0.3	1-dodecene	−0.8
trans-3-Hexene	−1.2	*cis*-3-hexene	0.0		
trans-3-Heptene	−0.9	*cis*-3-heptene	0.2		
trans-3-Octene	−0.8	*cis*-3-octene	−0.1		
trans-3-Nonene	−0.8	*cis*-3-nonene	−0.4		
trans-3-Decene	−0.8	*cis*-3-decene	−0.7		
trans-3-Undecene	−0.8	*cis*-3-undecene	−0.9		
trans-3-Dodecene	−0.8	*cis*-3-dodecene	−1.1		
trans-4-Octene	−0.9	*cis*-4-octene	−0.2		
trans-4-Nonene	−0.9	*cis*-4-nonene	−0.5		
trans-4-Decene	−0.9	*cis*-4-decene	−0.8		
trans-4-Undecene	−1.0	*cis*-4-undecene	−1.1		
trans-4-Dodecene	−1.1	*cis*-4-dodecene	−1.4		
trans-5-Decene	−0.9	*cis*-5-decene	−0.9		
trans-5-Undecene	−1.2	*cis*-5-undecene	−1.3		
trans-5-Dodecene	−1.3	*cis*-5-dodecene	−1.7		
trans-6-Dodecene	−1.4	*cis*-6-dodecene	−1.9		

A comparison of the ΔT_b values for the n-alkenes C_6–C_{11} shows certain regularities (Table III). It is apparent that the ΔT_b values within the individual series of *trans*-alkenes are very close to each other whereas the ΔT_b values for *cis*-alkenes as well as 1-alkenes are higher and decrease regularly with the number of carbon atoms.

Certain regularities in the deviations of ΔT_b for positional and geometrical isomers of an equal number of carbon atoms are evident from Table IV. One can see that the behaviour of the positional 2-isomers is different from the other positional isomers; the deviations show both positive and negative values, so that simple correlations will not render precise results. On the other hand, a knowledge of the deviations of ΔT_b with respect to the number of carbon atoms affords a relatively precise method of determining the boiling points of higher n-alkenes such as the dodecenes. The necessary δI values can be determined from the dependence of the structural increment H^S on the number of carbon atoms for the individual series

TABLE IV

SUMMARY OF THE ΔT_b VALUES *vs.* THE POSITION AND GEOMETRICAL ARRANGEMENT OF THE DOUBLE BOND AND THE NUMBER OF CARBON ATOMS OF *n*-ALKENES C_6–C_{12}

Number of C atoms	*trans-Alkene*	ΔT_b	*cis-Alkene*	ΔT_b	*1-Alkene*	ΔT_b
C_6	*trans*-2-	−0.2	*cis*-2-	1.4	1-	−0.2
	trans-3-	−1.2	*cis*-3-	0.0		
C_7	*trans*-2-	0.1	*cis*-2-	1.2	1-	−0.3
	trans-3-	−0.9	*cis*-3-	0.2		
C_8	*trans*-2-	0.0	*cis*-2-	0.8	1-	−0.4
	trans-3-	−0.8	*cis*-3-	−0.1		
	trans-4-	−0.9	*cis*-4-	−0.2		
C_9	*trans*-2-	0.0	*cis*-2-	0.5	1-	−0.5
	trans-3-	−0.8	*cis*-3-	−0.4		
	trans-4-	−0.9	*cis*-4-	−0.5		
C_{10}	*trans*-2-	0.0	*cis*-2-	0.2	1-	−0.6
	trans-3-	−0.8	*cis*-3-	−0.7		
	trans-4-	−0.9	*cis*-4-	−0.8		
	trans-5-	−0.9	*cis*-5-	−0.9		
C_{11}	*trans*-2-	0.0	*cis*-2-	0.0	1-	−0.7
	trans-3-	−0.8	*cis*-3-	−0.9		
	trans-4-	−1.0	*cis*-4-	−1.1		
	trans-5-	−1.2	*cis*-5-	−1.3		
C_{12}	*trans*-2-	0.0	*cis*-2-	−0.3	1-	−0.8
	trans-3-	−0.8	*cis*-3-	−1.1		
	trans-4-	−1.1	*cis*-4-	−1.4		
	trans-5-	−1.3	*cis*-5-	−1.7		
	trans-6-	−1.4	*cis*-6-	−1.9		

of *n*-alkenes[1–3]. By introducing the respective correction (*cf.* Table III), it is possible to calculate a boiling point identical to that calculated by eqn. 2.

Calculation from corrected index boiling points after MATUKUMA

MATUKUMA introduced[9] the following relation for calculating the index boiling point I_B:

$$I_B = 10^{(0.00134025T_b-2.558916)} - 440.5 \tag{4a}$$

which is calculated from the retention index of the substance, I_R ($I_R = I$), and from the known retention indices and boiling points of substances of the same structure but having one carbon atom less in the molecule, and with the aid of the so-called paraffinic concept $\Delta I_{R-B}{}^{(p)}$. For instance, for *cis*-2-dodecene (c-2-C_{12})

$$I_{B,c-2-C_{12}} = I_{c-2-C_{12}} - (I_{n-C_{12}} - I_{B,n-C_{12}}) + f_c \tag{4b}$$

where $\Delta I_{R-B}{}^{(p)}$ $(C_{12}) = (I_{n\text{-}C_{12}} - I_{B,n\text{-}C_{12}})$ is the difference between the retention index and the index boiling point of *n*-dodecane, and f_c is the correction factor for the calculation of the boiling point of *n*-dodecane from its retention index:

$$f_c = (I_{n-C_{11}} - I_{B,n-C_{11}}) - (I_{c-2-C_{11}} - I_{B,c-2-C_{11}}) \tag{4c}$$

TABLE V

VALUES OF DIFFERENCES (ΔT_b) IN THE BOILING POINTS CALCULATED BY EQNS. 4 AND 2 FOR C_6–C_{12} *n*-ALKENES

trans-Alkenes	ΔT_b	*cis-Alkenes*	ΔT_b	*1-Alkenes*	ΔT_b
trans-2-Heptene	0.26	*cis*-2-heptene	0.0	1-heptene	−0.1
trans-2-Octene	0.0	*cis*-2-octene	−0.3	1-octene	−0.1
trans-2-Nonene	0.0	*cis*-2-nonene	−0.2	1-nonene	−0.1
trans-2-Decene	0.0	*cis*-2-decene	−0.2	1-decene	−0.1
trans-2-Undecene	0.0	*cis*-2-undecene	−0.2	1-undecene	−0.1
trans-2-Dodecene	0.0	*cis*-2-dodecene	−0.2	1-dodecene	−0.1
trans-3-Heptene	0.1	*cis*-3-heptene	0.2		
trans-3-Octene	0.1	*cis*-3-octene	−0.3		
trans-3-Nonene	0.0	*cis*-3-nonene	−0.3		
trans-3-Decene	−0.1	*cis*-3-decene	−0.3		
trans-3-Undecene	0.0	*cis*-3-undecene	−0.2		
trans-3-Dodecene	0.0	*cis*-3-dodecene	−0.3		
trans-4-Octene	0.0	*cis*-4-octene	−0.3		
trans-4-Nonene	0.0	*cis*-4-nonene	−0.3		
trans-4-Decene	−0.1	*cis*-4-decene	−0.4		
trans-4-Undecene	0.0	*cis*-4-undecene	−0.4		
trans-4-Dodecene	−0.1	*cis*-4-dodecene	−0.4		
trans-5-Decene	−0.1	*cis*-5-decene	−0.4		
trans-5-Undecene	−0.2	*cis*-5-undecene	−0.4		
trans-5-Dodecene	−0.1	*cis*-5-dodecene	−0.4		
trans-6-Dodecene	−0.1	*cis*-6-dodecene	−0.4		

The above equations were used to calculate the I_B values for the individual *n*-dodecenes, while the f_c values were calculated from undecenes of equal structure. The calculated boiling points of *n*-dodecenes are summarized in Table II.

It was also found from the results for the *n*-dodecenes that the values of the factor f_c are constant only for the calculation with *trans*-alkenes, whereas the boiling points calculated for *cis*- and 1-alkenes are lower than the actual ones, since the f_c values for these types of alkene rise with the number of carbon atoms.

The deviations ΔT_b of the boiling points calculated by eqns. 4 and 2 are quoted, for the groups of C_6–C_{12} *trans*-, *cis*-, and 1-alkenes, in Table V. One can see a very good agreement between the boiling points calculated by eqns. 2 and 4 in the case of *trans*-alkenes as well as regular deviations for *cis*- and 1-alkenes. The maximum deviation is −0.4° with both methods. The values for *trans*-6- and *cis*-6-dodecenes of f_c cannot be directly calculated from eqn. 4 since these positional isomers do not exist with undecenes. The f_c values were therefore estimated by virtue of the regularity of the dependences of f_c on the position of the double bond[4].

REFERENCES

1 L. Soják and A. Bučinská, *J. Chromatogr.*, 51 (1970) 75.
2 L. Soják, P. Majer, P. Skalák and J. Janák, *J. Chromatogr.*, 65 (1972) 137.
3 L. Soják and J. Hrivňák, *J. Chromatogr. Sci.*, in press.
4 L. Soják, J. Krupčík, K. Tesařík and J. Janák, *J. Chromatogr.*, 65 (1972) 93.
5 F. Asinger, B. Fell and G. Steffan, *Chem. Ber.*, 97 (1964) 1955.
6 S. W. Ferris, *Handbook of Hydrocarbons*, Academic Press, New York, 1955.
7 J. H. Purnell, *Gas Chromatography*, J. Wiley, London, 1962, p. 39, 219.
8 D. H. Desty and B. H. Whyman, *Anal. Chem.*, 29 (1957) 320.
9 A. Matukuma, in C. L. A. Harbourn and R. Stock (Editors), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 55.