CHROM. 5613

GAS CHROMATOGRAPHIC IDENTIFICATION OF THE MAIN AROMATIC HYDROCARBONS FROM THE CATALYTIC DEHYDROGENATION OF *n*-UNDECANE

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SUMMARY

The C_{11}-alkylbenzene products from the dehydrogenation of *n*-undecane were identified on the basis of relations between the structure and retention indices using the linear correlations of free energies found for C_8–C_{10} methyl- and ethyl-monoalkylbenzenes separated on a squalane capillary column.

In a preceding paper[1], we discussed the separation of 43 theoretically existing C_6–C_{10} aromatics by means of open tubular columns coated with squalane and polyethylene glycol 400. It is rather difficult to extend this field to C_{11} aromatics because there exist 68 possible compounds (of which 50 are alkylaromatics). The published retention data for C_{11} aromatics are therefore very incomplete[2]. For the identification of the C_{11} aromatic products from the dehydrogenation of *n*-undecane, not only standards but also reference data were missing. The determination of retention data for C_{11} aromatics on the basis of the data for the C_6–C_{10} aromatics using the principle of additivity, based on empirical rules, was shown to be inaccurate (Table I).

The validity of the correlations existing between the structure of C_8–C_{10}-dialkyl derivatives of aromatic hydrocarbons and their retention data was therefore examined using linear correlations of free energy[3]. These relations were used for the identification of C_{11} alkylaromatics.

For the retention index of toluene, I_t, and substituted toluenes, I_x, the following relation was found by the method of least squares:

$$\log\left(\frac{I_t}{I_x}\right) = \varrho \cdot \tau_T + b \qquad (1)$$

TABLE I

CONTRIBUTION OF THE METHYLENE GROUP TO THE RETENTION INDICES OF ALKYLAROMATICS

Component	I^s_{115}	I_{CH_2}
Benzene	653.6	
		107.1
Toluene	760.7	
		90.6
Ethylbenzene	851.3	
		89.5
n-Propylbenzene	940.8	
		98.8
n-Butylbenzene	1039.6	
		98.0
n-Pentylbenzene	1137.6	
1-Methyl-2-methylbenzene	888.1	
		80.7
1-Methyl-2-ethylbenzene	968.8	
		81.7
1-Methyl-2-*n*-propylbenzene	1050.5	
		97.5
1-Methyl-2-*n*-butylbenzene	1148.0	
1-Ethyl-2-ethylbenzene	1043.6	
		78.7
1-Ethyl-2-*n*-propylbenzene	1122.3	

where τ_T is the substitution constant = $\log (T_t/T_x)$ which expresses the variations in the electron configurations of methylalkylaromatics (x) according to the reference standard toluene (t), T_t and T_x are the boiling points (°K) of toluene and the alkylaromatic, respectively, ϱ is the constant characterizing the liquid phase, and b is a constant independent of the electron shifts in the molecule.

By correlating the retention indices, I, and the substitution constant, τ_T, for *ortho-*, *meta-* and *para*-C_8-C_{10}-methylaromatics using eqn. 1, arranged into the form:

$$\log T_x = \log T_t - \frac{1}{\varrho}\left(\log\left(\frac{I_t}{I_x}\right) - b\right) \qquad (2)$$

the boiling points of the alkylaromatics, which separate on a squalane column at 115°, were calculated. The values of the constants were $\varrho = 1.8224$ and $b = -0.0001$. The boiling points of the aromatics were calculated with an accuracy of ±0.3°K.

TABLE II

LITERATURE AND CALCULATED BOILING POINTS OF MAIN CHARACTERISTIC C_{11} ALKYLAROMATICS AND THEIR RETENTION INDICES ON SQUALANE AT 86, 100, 115 AND 130°C

Component	Literature b.p. (°C)	Calculated b.p. (°C)	I^s_{86}	I^s_{100}	I^s_{115}	I^s_{130}	$10\left(\frac{\delta I^s}{\delta T}\right)$
1-Ethyl-2-*n*-propylbenzene	203	202.1	1113.9	1118.1	1122.3	1126.9	2.90
n-Pentylbenzene	205.5	205.6	1129.5	1133.5	1137.6	1142.3	2.78
1-Methyl-2-*n*-butylbenzene	208	207.9	1139.1	1143.7	1148.0	1152.8	3.06

On the basis of the retention indices determined for the aromatics produced from the dehydrogenation of n-undecane, eqn. 2 was used to calculate the corresponding boiling points in °K. The values determined were converted into °C and compared with the published data for the C_{11} alkylaromatics[4]. From these data and the mechanism of dehydrogenation of C_6–C_{10} n-alkanes to aromatics[5], the alkylaromatics in the C_{11} dehydrogenation product were identified. The results are given in Table II.

These calculations confirm the identification of 1-methyl-2-n-butylbenzene because this is an alkyl-substituted toluene. The identification of 1-ethyl-2-n-propylbenzene was confirmed by the correlation of the retention index of ethylbenzene, I_{eb}, and the retention index of alkylsubstituted ethylbenzenes, I_x, with the chromatographic substitution constant, $\tau_T = \log\left(\frac{T_{eb}}{T_x}\right)$ ($\varrho = 1.8195$, $b = -0.0019$, standard deviation of $T_x = \pm 0.2$°K). The calculated boiling point for 1-ethyl-2-n-propylbenzene was $T_x = 202.2°$.

In the case of n-propyl derivatives, a decrease in the increment values was observed, caused by a tendency towards ring conformation. Similar anomalies were observed with alkenes with similar structures suitable for ring conformation, *e.g.*, *trans*-2-hexene[6] and *trans*-3-heptene[6]. The constant incremental contribution to the retention index of the methylene group in the n-alkyl chain of aromatics becomes evident from n-pentylbenzene (Table I).

The calculated changes in the retention indices with temperature on the squalane column for the C_{11} alkylaromatics are in Table II, $10(\partial I/\partial T) = 2.78$ to 3.06, are approximately equal to the corresponding values for C_{10} aromatics resulting from dehydrogenation[3].

The aromatic products formed as in impurities in straight-chain undecenes[7] during the catalytic dehydrogenation of n-undecane are mainly *ortho*-derivatives of toluene, ethylbenzene and n-alkylbenzene. This composition presupposes the formation of the aromatics by the dehydrocyclization of alkenes that have a double bond in various positions, and not by the direct dehydrocyclization of the n-alkanes. This type of reaction is specific for a certain type of oxide catalyst.

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