

Identification of Non-branched Alkenylcycloalkanes With a Terminal Double Bond from Retention Index Increments

G. Anders* / K. Anders

Akademie der Wissenschaften der DDR, Zentralinstitut für Organische Chemie, Bereich Organische Grundstoffe, DDR-7050 Leipzig, Permoserstraße 15, G.D.R.

W. Engewald

Karl-Marx-Universität Leipzig, Sektion Chemie, DDR-7010 Leipzig, Liebigstraße 18, G.D.R.

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Summary

Reaction products of the pyrolysis of n-dodecylpentane and n-hexylcyclohexane had been separated and identified on a glass capillary column coated with Polydimethylsiloxane OV-1.

The identification of the components in the pyrolysis products and of the corresponding hydrogenated samples was performed from structure retention correlations, especially retention index increments (I_{CH_2}), homomorphy values (H^{OV-1}) and the temperature coefficients of retention indices ($\delta I/\delta T$). Hence the presence of homologous 1-alkenes and of monoalkenylcycloalkanes could be confirmed. Based on the addition principle of index increments the determination of the side chain structure of alkenylcycloalkanes (straight chain) and the position of the double bond was ascertained. The calculation of the retention indices of these compounds was performed with high accuracy (deviation < 1 index unit). Retention indices of 10 1-alkenes, 11 monoalkenylcyclopentanes, 11 monoalkylcyclopentanes, 5 monoalkenylcyclohexanes and 5 monoalkylcyclohexanes were determined on the liquid phase Polydimethylsiloxane OV-1.

Introduction

The shortage in crude oil production needs the conversion of higher boiling fractions to petrochemicals. Under these circumstances higher boiling hydrocarbons become more important as feedstock in industrial pyrolysis plants.

Because these fractions are containing a variety of special structured hydrocarbons we are interested in the thermal decomposition of alkylcycloalkanes [1].

But the analysis and the identification of reaction products, required for mechanistic and kinetic considerations, are difficult because of their complexity, the lack of standard compounds and retention data, especially in the case of higher boiling hydrocarbons.

This paper is concerned with the capillary gas chromatographic investigation of reaction mixtures obtained by thermal decomposition of n-dodecylcyclopentane and n-hexylcyclohexane. From mechanistic considerations non-branched 1-alkenes and mono-alkenylcycloalkanes are expected as main reaction products.

Regarding the hydrocarbons the Kováts retention index is the most reliable parameter for chromatographic identification, especially in combination with mass spectra. In the literature retention indices of 1-alkenes on different liquid phases are available [2, 3, 4], whereas only few values of alkenylcycloalkanes with short side chains are published [5].

The separation and quantitative analysis was performed by isothermal and temperature programmed GC on a glass capillary column coated with Polydimethylsiloxane OV-1 as stationary phase. The identification of the above mentioned compounds in the complex mixtures could be achieved by utilization of structure retention correlations based on retention index increments.

The proposed structures could be verified in some cases using GC-MS combination.

Experimental

The gas chromatographic measurements were performed on a Fractovap 2400 T chromatograph (Carlo Erba Strumentazione), equipped with a flame-ionization detector and a sampling splitter.

An open-tubular column (55m \times 0.21mm) manufactured from soda-lime glass (Jenaer Gerätglas 16/III) was used.

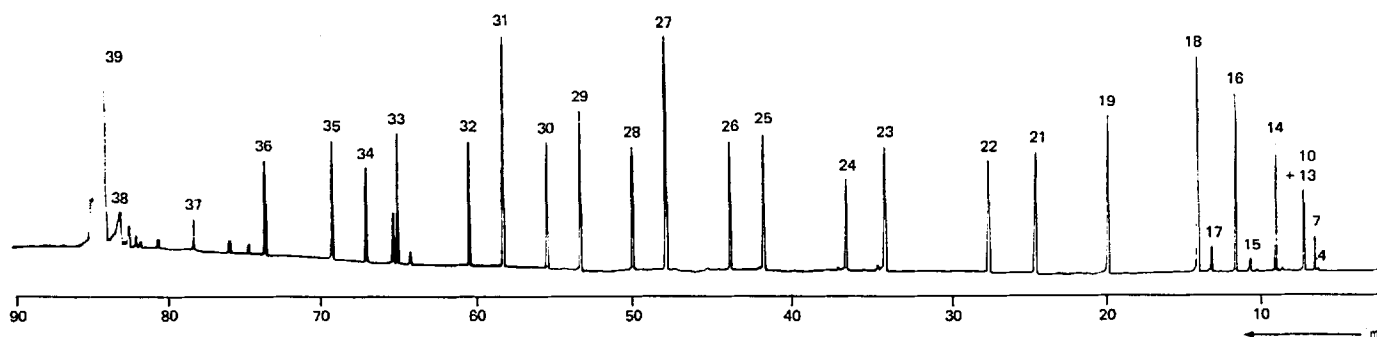


Fig. 1

Gas chromatogram of the products of dodecylcyclopentane pyrolysis

Column: OV-1 (55m X 0.2mm), temperature programmed from 30 to 220°C at 3K/min, Numbered peaks are referred to compounds listed in Table I and IV.

After pretreatment of the inner surface by BaCO₃ precipitation and subsequent deactivation with Carbowax 20 M [6] the capillary column was coated with OV-1 as liquid phase by the static method [7]. The film thickness are calculated to 0.35 μm. The k' value for n-nonane at 90°C was 10.4, while the HETP value was 0.27 mm. Nitrogen was used as the carrier gas.

The determination of the retention times was performed with a Hewlett Packard 3370 B digital integrator. The gas hold up (mobil time) was calculated by extrapolation from the retention times of n-alkanes. The Kováts retention indices represent the average of at least four determinations for each compound. The standard deviation of the retention index estimation was ± 0.3 index units abs..

The hydrogenation of samples was carried out on a nickel catalyst at 200°C and a hydrogen pressure of 5 MPa.

Results and Discussion

Comparing the chromatograms of the original reaction products with those of the corresponding hydrogenated samples it can be concluded, that the thermal decomposition of monoalkylcycloalkanes yields mainly unsaturated

hydrocarbons. The chromatogram of the products of dodecylcyclopentane pyrolysis is shown in Fig. 1.

The presence of homologous 1-alkenes could be confirmed by comparison of estimated retention index values and their temperature coefficients with those of standard compounds and literature values [2, 3, 4], by massspectrometric determination of the molecular weight values and the origin of alkanes after hydrogenation. The estimated retention values of the identified 1-alkenes are listed in Table I. The identification of the other, still unknown components in the reaction products and the corresponding hydrogenated samples was performed by utilization of structure retention correlations, especially retention index increments:

- (a) The index differences of the consecutive main peaks are formed and plotted versus the number of carbon atoms in the side chain.

In the case of $n > 4$ the index differences represents a constant value, near to 100, what is characteristic for homologous series:

$$I_{CH_2} = I_{R-(CH_2)_n-H} - I_{R-(CH_2)_{n-1}-H}$$

- (b) The differences of retention indices between the compounds, to be identified, and the n-alkanes of the same carbon number are formed and plotted versus the carbon number of the side chain:

$$H^{OV-1} = I_{substance} - I_{n-alkane}$$

In all cases one obtains positive values, corresponding with known values of cyclic hydrocarbons.

After the hydrogenation the H^{OV-1}-values of the components to be identified are 12 index units higher. This difference points to terminal double binding.

Based on the additivity of index increments the Kováts retention indices of the alkenylcycloalkanes are precalculated:

$$I^{OV-1} = 100n + \sum H_i^{OV-1} = 100n + H_{double\ bond}^{OV-1} + H_{alkylcycloalkanes}^{OV-1}$$

Table I. Retention indices (I₁₀₀) and index increments (H^{OV-1}) of 1-alkenes on methylsilicone OV-1.

No.	Hydrocarbon	I ₁₀₀ ^{OV-1} (exp.)	δI/K	Temp. range (°C)	H ^{OV-1}
10	1-Butene	388,7	—	—	-11,3
14	1-Pentene	488,8	-0,0045	30-90	-11,2
18	1-Hexene	588,9	0,001	30-110	-11,1
21	1-Heptene	689,0	0,0095	30-130	-11,0
23	1-Octene	789,0	0,0150	50-130	-11,0
25	1-Nonene	888,7	0,0100	50-130	-11,3
27	1-Decene	988,6	0,0155	70-130	-11,4
29	1-Undecene	1088,0	0,0225	90-130	-12,0
31	1-Dodecene	1187,9	0,0081	90-130	-12,1
34	1-Tetradecene	1387,9	0,0250	190-210	-12,1

Table II. Retention indices (I_{100}) and index increments (H^{OV-1}) of *n*-alkylcyclopentanes and *n*-alkylcyclohexanes on methylsilicone OV-1.

Hydrocarbon	I_{100}^{OV-1} (exp.)	$\delta I/K$	Temp. range (°C)	H^{OV-1}
Cyclopentane	574,5	0,170	70–110	74,5
Methylcyclopentane	638,1	0,199	70–130	38,1
Ethylcyclopentane	743,4	0,226	70–150	43,4
Propylcyclopentane	839,2	0,232	70–170	39,2
Butylcyclopentane	938,3	0,241	90–190	38,3
Pentylcyclopentane	1037,6	0,253	110–210	37,6
Hexylcyclopentane	1137,9	0,249	110–210	37,9
Octylcyclopentane	1038,0	0,262	150–210	38,0
Nonylcyclopentane	1438,0	0,263	150–210	38,0
Decylcyclopentane	1536,3	0,283	170–210	36,3
Undecylcyclopentane	1636,4	0,288	170–210	36,4
Cyclohexane	673,6	0,248	30– 90	73,6
Methylcyclohexane	734,6	0,268	50– 90	34,6
Ethylcyclohexane	842,8	0,290	50– 90	42,8
Propylcyclohexane	936,4	0,280	50– 90	36,4
Butylcyclohexane	1036,0	–	–	36,0

The values $H_{alkylcycloalkanes}^{OV-1}$ were determined from experimentally obtained retention indices of alkylcycloalkanes (see Table II).

As an example the structure of the alkyl side chain and the position of the double bond in the chain was proved for pentenylcyclopentanes (see Table III).

If using straight chain 1-alkenes for the index calculation one observes the smallest deviations (ΔI) between calculated and experimentally determined retention indices. So it was confirmed that the discussed compounds possess non-branched alkenyl side chains with terminal double bond.

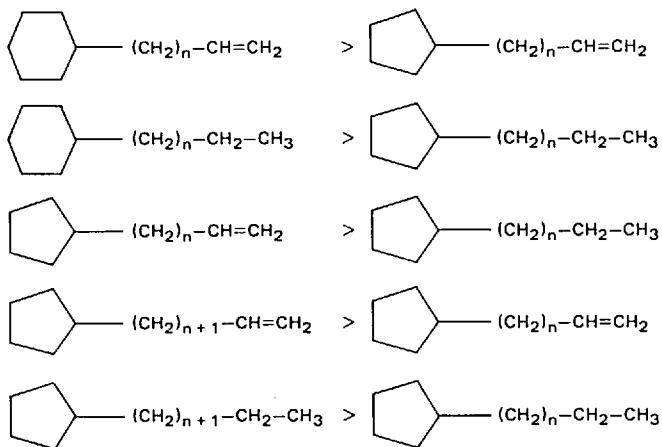
Based on the experimentally determined retention indices of the monoalkylcycloalkanes (Table II) and the 1-alkenes (Table I) the corresponding values of alkenylcycloalkanes (I_{calc}^{OV-1}) are calculated and compared with the experimentally determined values (Table IV).

As a rule the deviations (ΔI) between the experimentally obtained and the calculated values are smaller than one index unit.

In summary the data demonstrate the utility of index increments for the identification of complicated hydrocarbon structures.

Considering the temperature dependence of the retention indices of the 3 discussed structure groups (1-alkenes, alkylcycloalkanes, alkenylcycloalkanes) regarding the 1-alkenes there is a good agreement with values from literature for apolar liquid phases [2, 4]. There were found small positive temperature coefficients.

But regarding the alkenylcycloalkanes and the alkylcycloalkanes [10, 11, 12] the temperature dependence is stronger, what is in agreement with the theory of Hively and Hinton [8]. The order of temperature dependence of the identified alkenyl- and alkylcycloalkanes was determined as follows.



The increasing of the $\delta I/\delta T$ -values in a homologous series was also found by Dielmann [9].

In Fig. 2 and 3 are demonstrated the dependence of index increments (I_{CH_2} and H^{OV-1}) on the number of carbon atoms in the side chain.

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Table III. Precalculated Retention Indices (I_{100}) of pentenylcyclopentane on methylsilicone OV-1.
 I_{100}^{OV-1} (exp.) = 1026,5

Pentene	$H_{pentene}^{OV-1}$	$H_{alkylcyclopentene}^{OV-1}$	I_{100}^{OV-1} pentenylcyclopentane
1-Pentene	– 11,2	37,6	1026,4
trans-2-Pentene	4,5	37,6	1042,1
cis-2-Pentene	14,8	37,6	1052,4
2-Methyl-1-Butene	– 5,2	37,6	1032,4
2-Methyl-2-Butene	19,7	37,6	1057,3
3-Methyl-1-Butene	– 42,6 ^a	19,9 ^a	977,3 ^a

^a = values for 30°C column temperature

Table IV. Retention indices (I_{100}) and index increments (H^{OV-1}) of n-alkenylcycloalkanes and n-alkenylcyclohexanes on methylsilicone OV-1.

No.	Hydrocarbon	I_{100}^{OV-1} (calc.)	I_{100}^{OV-1} (exp.)	$\delta I/K$	Temp. range (°C)	H^{OV-1}
19	Methylenecyclopentane	—	578,5	0,193	70–130	58,5
22	Vinylcyclopentane	—	731,3	0,234	70–150	31,3
24	Allylcyclopentane	—	828,8	0,242	70–150	28,8
26	4-Butenylcyclopentane	927,0	927,7	0,254	90–170	27,7
28	5-Pentenylcyclopentane	1026,4	1026,5	0,263	110–190	26,5
30	6-Hexenylcyclopentane	1126,8	1125,9	0,274	110–210	25,9
32	7-Heptenylcyclopentane	—	1224,7	0,270	130–210	24,7
33	8-Octenylcyclopentane	1327,0	1325,9	0,286	150–210	25,9
35	9-Nonenylcyclopentane	1426,7	1426,5	0,283	150–210	26,5
36	10-Decenylcyclopentane	1524,9	1524,7	0,305	170–210	24,7
37	11-Undecenylcyclopentane	1624,4	1625,3	0,305	170–210	25,3
	Methylenecyclohexane	—	750,8	0,271	60–130	50,8
	Vinylcyclohexane	—	829,8	0,311	60–130	29,8
	Allylcyclohexane	—	925,8	0,323	60–130	25,8
	4-Butenylcyclohexane	1024,7	1024,5	0,325	90–130	24,5
	5-Pentenylcyclohexane	—	1123,9	0,308	90–130	23,9

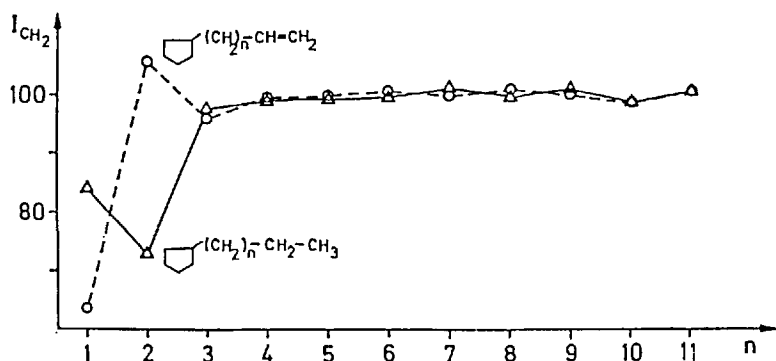


Fig. 2
Dependence of the index increments I_{CH_2} on the number of carbon atoms in the side chain

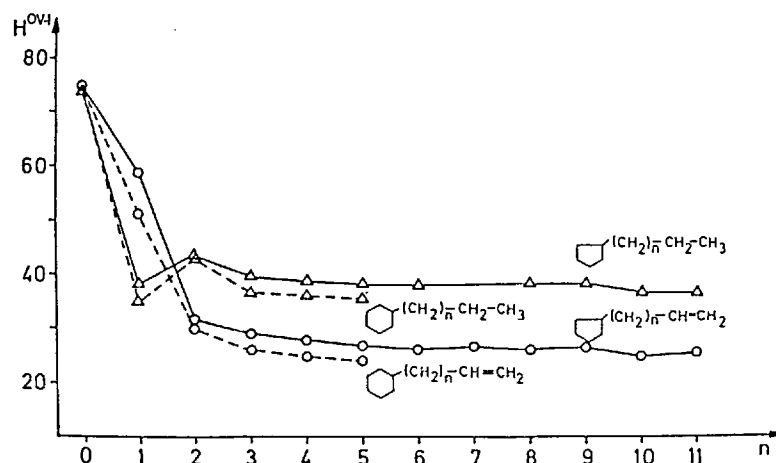


Fig. 3
Dependence of the index increments H^{OV-1} on the number of carbon atoms in the side chain

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