

GAS CHROMATOGRAPHY WITH
STATIONARY PHASES CONTAINING SILVER NITRATEIII. ISOMERIC C₈ AND C₉ CYCLOHEXENES
AND *p*-MENTHENES*

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Gas chromatography with silver nitrate-glycol solutions as the stationary phase is a method of choice for the rapid and accurate analysis of closely boiling cyclic olefins. In earlier work^{1,2} on the use of this phase we have reported on the separation of the methylcyclohexenes and of the methyl- and ethylcyclopentene series of isomers. The usefulness of the method has been demonstrated by its application to equilibrium studies^{3,4}.

In the present investigation the study of the relationship between structure and retention volume has been extended to higher homologues (C₈ — C₁₀ olefins), containing a six-membered ring and 2-4 carbons in side chains. Types of compounds not examined so far, *e.g.* olefins with a tetrasubstituted double bond and derivatives with two side chains (*p*-menthenes), were included in the study.

The relative retention volumes of the compounds were determined by the procedure described previously^{1,2}. However, whereas for the lower homologues a saturated silver nitrate solution has been employed as column liquid, it was found necessary in the present case to use a concentration of no more than 30% and to reduce the ratio of liquid to support from 1:2 to 1:3 in order to avoid unduly high retention times. Thus, even the *p*-menthenes, which boil between 167-175°, could be chromatographed under the experimental conditions in about 45 min. It is to be noted that reducing the retention time by raising the column temperature is limited by the instability of the phase above 40°.

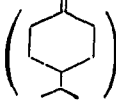
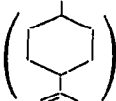
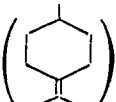
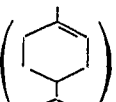
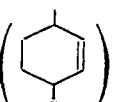
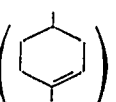
The results are given in Table I. With the exception of 3- and 4-ethylcyclohexene (IV and V, respectively) and of 4(8)- and 1-*p*-menthene (XII and XIII, respectively), the retention volumes were found to differ sufficiently to permit easy separation of isomers. Thus, ethylidenecyclohexane (II) and 1-ethylcyclohexene (III), which boil only 0.5° apart, have retention volumes differing by about 100%. High selectivity (ratio of retention volumes of ~ 1:4) was observed also in the case of 1- and 4-isopropylcyclohexene (VII and IX, respectively) and in the separation of 1- from 1(7)-*p*-menthene (XIII and X, respectively).

* Part of a thesis presented by J. HERLING to the Hebrew University, Jerusalem, in partial fulfilment of the requirements for the degree of Ph.D. References 1 and 2 are to be considered as Parts I and II, respectively, of this series.

SAUVAGE⁵ has determined the retention volumes of the *p*-menthenes with a saturated silver nitrate solution in diethylene glycol at 60° and has found a similar relative order for the various isomers. An exact correspondence with the present results, however, cannot be expected because of the difference in conditions.

In order to improve the separation of 3- from 4-ethylcyclohexene, the effect of other solvents and of temperature on the chromatographic behaviour of the isomeric C₈ cyclohexenes was investigated. The results are summarized in Table II.

TABLE I
RETENTION VOLUMES* OF C₈-C₁₀ CYCLOHEXENES
ON A SILVER NITRATE-GLYCOL SOLUTION**

No.	Compound	B.p.(°C)/760 mm	r*** at 30°
I	Vinylcyclohexane	127.0	3.72
II	Ethylidenecyclohexane	136.8	1.70
III	1-Ethylcyclohexene	136.3	0.85
IV	3-Ethylcyclohexene	134.5	2.43
V	4-Ethylcyclohexene	132.5	2.37
VI	Isopropylidenecyclohexane	160.5	1.51
VII	1-Isopropylcyclohexene	155.0	1.00
VIII	3-Isopropylcyclohexene	149.6	2.70
IX	4-Isopropylcyclohexene	154.0	3.85
X	1(7)- <i>p</i> -Menthene 	174.0	8.17
XI	8- <i>p</i> -Menthene 	168.5	4.34
XII	4(8)- <i>p</i> -Menthene 	173.0	1.92
XIII	1- <i>p</i> -Menthene 	174.5	2.03
XIV	<i>trans</i> -2- <i>p</i> -Menthene 	166.6	3.17
XV	3- <i>p</i> -Menthene 	175.0	1.21

* Relative to toluene.

** Concentration of silver nitrate/glycol 3 g/10 ml; column length 2 m; weight ratio of solid support^{1,2} to liquid phase 3:1.

*** Helium flow rate (ml/min): I-V, 60; VI-IX, 52; X-XV, 46.

It was found that benzyl cyanide and triethylene glycol reduce the selectivity of the liquid phase. On the other hand, the lowering of the column temperature from 30 to 21° increases the difference in the retention volumes of the 3- and 4-isomers from 2.5% to about 7%. Even at the lower temperature, however, there is still some overlapping of the peaks. The two components could be determined with a relative error of 2–2.5%, as evidenced by experiments with synthetic mixtures. The decrease of temperature also improves the separation of the remaining C₈ isomers (see Table II), which can be analysed quantitatively with an accuracy of about 1%.

TABLE II
RETENTION VOLUMES* OF C₈ CYCLOHEXENES ON SILVER NITRATE SOLUTIONS**
AT DIFFERENT TEMPERATURES

Compound	21°		30°			40°		
	A	B	A	B	C	A	B	C
I Vinylcyclohexane	4.47	—	3.72	1.12	1.28	3.09	1.00	1.13
II Ethylidenecyclohexane	2.03	1.00	1.70	1.00	0.75	1.47	0.84	0.70
III 1-Ethylcyclohexene	0.93	0.75	0.85	0.74	0.50	0.77	0.67	0.50
IV 3-Ethylcyclohexene	2.87	1.14	2.43	1.12	1.00	2.04	1.00	0.95
V 4-Ethylcyclohexene	2.67	1.13	2.37	1.12	1.00	2.04	1.00	0.95

* Relative to toluene.

** A = 3 g AgNO₃/10 ml ethylene glycol; B = 3 g AgNO₃/10 ml benzyl cyanide; C = 3 g AgNO₃/10 ml triethylene glycol.

DISCUSSION OF RESULTS

It can be shown⁶ that in the case of olefins, forming a 1:1 complex with silver ion, the partition coefficient k , which determines the magnitude of the retention volume, is expressed by:

$$k = k_0(1 + [\text{Ag}^+]K)$$

where:

k_0 = partition coefficient of the olefin between the solvent and the gas phase;

K = stability constant of the silver ion–olefin complex;

$[\text{Ag}^+]$ = concentration of silver ion (mole/l).

The measurement of partition coefficients and stability constants for a series of olefins will be the subject of a forthcoming publication. In the absence of information on these parameters, rules on the dependence of retention volume on structure can be established by limiting the comparisons to isomers. It can be assumed in this case that differences in retention volumes are determined to a first approximation by variation in the stability of the olefin–silver ion complexes. Thus, the following conclusions can be drawn from the data given in Table I:

(a) In all groups of endocyclic isomers the 1-alkyl compound has a lower retention volume than the 3- and 4-alkyl isomers (r of III < IV, V; r of VII < VIII, IX; r of XIII, XV < XIV). Analogous findings have been reported previously for the methylcyclohexenes¹ and for the methyl- and ethylcyclopentenes². Introduction of an additional substituent at the double bond results in a further decrease in relative retention. Thus, it has been found⁷, that 1,2-dimethylcyclohexene has a lower reten-

tion volume than 2,3-dimethylcyclohexene. This effect is readily explained by the strong influence of steric hindrance⁶ on the ease of formation of silver ion-olefin complexes.

As in the case of the endocyclic olefins, substitution of a semicyclic double bond greatly reduces the retention volume. For instance, when 1(7)-*p*-menthene (X) is compared with 4(8)-*p*-menthene (XII), in which the semicyclic double bond is substituted by two methyl groups, it is seen that the relative retention volume drops steeply from 8.17 to 1.92.

(b) Comparison of the data for the 3- and 4-isomers in the series of the methylcyclohexenes¹ and methyl- and ethyl-cyclopentenes² led to the conclusion that electronic effects enhance the relative stability of the complexes formed with the 3-alkyl isomers. The present data show, however, that for the ethylcyclohexenes the difference between the retention volumes of the two isomers (IV and V, respectively) becomes negligible, and that in the case of the isopropylcyclohexenes the order is sharply reversed (r of the 3-isomer (VIII) 2.70, as compared with r of the 4-isomer (IX) 3.85). The observed decrease in retention volume of the 3-isomer, as compared with the corresponding 4-isomer, can be understood from a consideration of models, which shows increasing steric hindrance of the double bond, as the substituent in the 3-position is enlarged.

The influence of the size of the alkyl group is further exemplified by the lower retention volume of 3-*p*-menthene (XV, r 1.21) as compared with 1-*p*-menthene (XIII, r 2.03).

(c) Comparison of isomers, in which the double bond is found respectively in an *endo* and a *semicyclic* position, are complicated by the simultaneous change of a number of structural factors. It has been reported previously¹ that methylenecyclohexane has a far higher retention volume than the methylcyclohexenes, and the same holds for 1(7)-*p*-menthene (X), as compared with the other menthenes. It is thus apparent that in the cyclohexane series the non-substituted *semicyclic* double bond has a considerably stronger tendency for complex formation than a non-substituted *endocyclic* one.

Comparison of similar pairs of semi- and endocyclic isomers in the cyclohexane series on the one hand and the cyclopentane series² on the other, shows considerable differences in the relative values of the retention volumes. Whereas 1-ethylcyclohexene (III) has only half the retention volume of ethylenecyclohexane (II), the reverse was found² in the case of 1-ethylcyclopentene, as compared with ethylenecyclopentane (r 1.30 and 0.68, respectively; measured on a saturated silver nitrate-glycol solution). This is in accordance with the considerably higher tendency for complex formation exhibited⁸ by endocyclic olefins having a five-membered as compared with a six-membered ring.

EXPERIMENTAL

Apparatus and procedure

A Perkin-Elmer Model 154 Fractometer was used in the experiments. The procedure was essentially the same as employed previously^{1,2}. Solutions, containing 30% of silver nitrate in different solvents (see Tables) were used as stationary phases. Toluene served as the internal standard throughout.

Source and preparation of materials

The olefins I–IX were obtained from the corresponding alcohols or acetates, with the exception of the 3-alkylcyclohexenes (IV, VIII), which were synthesized by condensation of the appropriate alkylmagnesium bromides with 3-bromocyclohexene. Details on the preparation and properties of 3- and 4-ethylcyclohexene and 3- and 4-isopropylcyclohexene are given elsewhere⁹. A brief outline of the preparation of the remaining C₈ and C₉ cyclohexenes is given below. The *p*-menthenes were synthesized⁵ in the Chemistry Dept., Northwestern University, Evanston, Ill., U.S.A. The compounds were purified to a degree as high as 98–99% in some cases, where they served also as samples for the measurement of infrared absorption spectra⁹.

Vinylcyclohexane (I) and ethylenecyclohexane (II). A mixture containing 68% of (I) and 32% of (II) was obtained, according to VAN DER BIJ AND KOOYMAN¹⁰, by pyrolysis at 450° of cyclohexylmethylcarbonyl acetate in a pyrex tube of 20 mm diameter and 40 cm length, filled with pyrex beads. The two hydrocarbons were separated by fractionation on a Piros-Glover spinning band column. 1 ml distillate of (I) was then subjected in batches to preparative gas chromatography on a column of 10 mm diameter and 2 m length, containing a saturated silver nitrate–glycol solution, as the stationary phase. The resulting sample had a purity of 99%, as determined by G.L.P.C. B.p. (determined by micro method¹¹) 127.0° (760 mm); n_{20}^D 1.4439 (reported¹⁰ 127.0°; n_{20}^D 1.4462). A sample of (II) of about 98% purity was obtained similarly by preparative G.L.P.C. B.p. 136.8° (760 mm); n_{20}^D 1.4623 (reported¹⁰ 136.8°; 1.4623).

1-Ethylcyclohexene (III). 1-Ethylcyclohexanol was dehydrated by refluxing in the presence of dilute sulphuric acid to give a mixture containing 92% of (III) and 8% of (II). The reaction product was fractionated and 1 ml of the distillate, enriched in (III), was subjected to additional purification by preparative G.L.P.C., as above. A sample of (III) of about 99% purity was obtained by this procedure. B.p. 136.3° (760 mm); n_{20}^D 1.4558 (reported¹² 136.0°; n_{20}^D 1.4575).

Isopropylidenecyclohexane (VI) and 1-isopropylcyclohexene (VII). A mixture, containing about 24% of (VI) and 76% of (VII), was prepared by dehydration of 1-isopropylcyclohexanol (b.p. 94° (23 mm); n_{20}^D 1.4579) with dilute sulphuric acid. After repeated fractional distillation two enriched samples were obtained, containing, respectively, 75% of (VI) and 90% of (VII).

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SUMMARY

Retention volumes of isomeric C₈ and C₉ cyclohexenes and *p*-menthenes have been determined, using stationary phases containing silver nitrate. As in the case of lower cyclic olefins, it is found that closely boiling isomers can be separated and determined quantitatively on a 30% silver nitrate–glycol solution at 20–30°. The correlation between olefin structure and retention volume is discussed.

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